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The Chemistry of Rhenium (V) Chloride

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THE CHEMISTRY OF

RHENIUM(V) CHLORIDE

BY

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RHENIUM(V) CHLORIDE

This dissertation is approved as a creditable and independent investigation by a candidate for the degree, Doctor of Philosophy, and is acceptable as meeting the dissertation requirements for the degree, but without implying that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis adviser Date

Head, Chemistry Department Date

THE CHEMISTRY OF RHENIUM(V) CHLORIDE

Abstract

GEORGE WARREN EASTLAND, JR.

Under the Supervision of Dr. Henry Gehrke, Jr.

Reactions of rhenium(V) chloride with triphenylphosphine, triphenylphosphine oxide, and pyridine were investigated, using various solvents. It was found that both the amount of water present and the age of the rhenium(V) chloride played important roles in determining the products formed.

The number and kind of products varied with the solvent used, with the more polar solvents giving mostly or all monomeric species. Rhenium(V) chloride and triphenylphosphine in acetonitrile gave tetrachlorobis(triphenylphosphine)rhenium(IV). Rhenium(V) chloride in anhydrous acetone reacted with pyridine to give dioxotetrakis-(pyridine)rhenium(V) chloride dihydrate. Sources for the oxygen and water in the complex are considered.

Nonpolar solvents allowed the formation of strong rhenium-to-rhenium bonds. Rhenium(V) chloride and triphenylphosphine in benzene gave bis(triphenylphosphonium) nonachlorodirhenate(III-IV) and trichloro(triphenylphosphine)rhenium(III).

Acetone proved to be an unusual case. Oxotrichlorobis-(triphenylphosphine)rhenium(V) and tetrachlorobis(triphenylphosphine)-

rhenium(IV) were obtained as initial precipitates in varying yields, depending upon reaction conditions. From the mother liquor was obtained 1,1-dimethyl-3-oxobutyltriphenylphosphonium pentachlorotriphenylphosphinerhenate(IV) and a mixture of bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) nonachlorodirhenate(III-IV) and bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) octachlorodirhenate(III). Independent methods of syntheses of these compounds were devised to verify their identity. Triphenylphosphine oxide and rhenium(V) chloride in acetone gave an unusual hydrogen-bonded compound, bis[μ-hydrogen-bis(triphenylphosphine oxide)] nonachlorodirhenate(III-IV).

The reaction of oxotrichlorobis(triphenylphosphine)rhenium(V) with hydrogen chloride in acetone led to the isolation of bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) hexachlororhenate(IV). The cation moeity was independently synthesized and isolated as the dihydrogen salt by the reaction of mesityl oxide, hydrogen chloride, and triphenylphosphine. The infrared and nmr spectra of the compounds are discussed.

The infrared spectra of a series of hexachlororhenate(IV) salts were recorded from 350-250 cm^{-1}. The position of the asymmetric rhenium-chlorine stretching mode was found to be dependent upon the counter-ion. Various factors leading to the asymmetric shape of

the band peak are discussed. Comparison to literature values are made and conclusions are drawn to explain the differences.

ACKNOWLEDGEMENTS

To Dr. Gehrke who, like all great teachers, gave more than he got;

To my parents, who have always been with me;

To the many others here, too numerous to enumerate, who have dedicated themselves to building a better school with students such as myself the fortunate beneficiaries;

And mostly,

To Judy, without whom this would not have been written;

I have, in the words of Shakespeare, "great cause to give great thanks."

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INTRODUCTION

Interest in rhenium chemistry, and particularly the coordination chemistry of rhnium, has increased tremendously since 1960. However, rhenium(V) chloride has found little use as a starting material. The main reason is the difficulty in handling the extremely hydroscopic rhenium(V) chloride.

The purpose of the project was to investigate the chemistry of rhenium(V) chloride. The initial system studied was the reaction of rhenium(V) chloride with triphenylphosphine in acetone. This system was chosen for two reasons. First, several studies concerning rhenium-triphenylphosphine compounds had been undertaken and these compounds had been well characterized. Secondly, the choice of the oxygenated solvent, acetone, could lead to oxygen abstraction by the rhenium. Impetus for this idea was provided by the observation that in the preparation of oxotrichlorobis(triphenylphosphine)rhenium(V), $ReOCl_3[P(C_6H_5)_3]_2$, from the reaction of triphenylphosphine, hydrochloric acid, and sodium perrhenate in ethanol, oxygen was present in the product (1). This is in light of the propensity of triphenylphosphine for oxygen. Similar inorganic chloride compounds, such as molybdenum(V) chloride, $MoCl_5$, are known to abstract oxygen from solvents and ligands containing oxygen (2).

The reactions of triphenylphosphine in non-oxygenated solvents, both polar and non-polar, were to be examined to complement the study and further elucidate the chemistry of rhenium(V) chloride.

It was also intended to study the reaction of rhenium(V) chloride with such ligands as pyridine and triphenylphosphine oxide. Some work on the pyridine system had been reported but the nature of the products was not fully established. The triphenylphosphine oxide-rhenium(V) chloride system had not been studied, and oxygen abstraction by the rhenium was possible.

Failure to characterize two of the reaction products required extension of the project to include the preparation of several new phosphonium salts. From this, the preparation and a study of the far infrared spectra of a series of hexachlororhenate(IV) salts ensued.

HISTORICAL SECTION

There exist several good reviews (3), (4), and (5) covering the entire realm of rhenium chemistry and so the Historical Section will be limited to a discussion of the history of rhenium(V) chloride, its chemistry, and systems necessary to elucidate reaction products.

Following the discovery of rhenium, one of the early interests centered around the various chlorides reported to be formed by the direct interaction of rhenium and chlorine. During a period of six years, from Noddack's initial report in 1928 to Geilmann's preparation and characterization of rhenium(V) chloride, there was considerable dispute regarding the nature of the products. These have been summarized in Table I. Since then, additional methods of preparing rhenium(V) chloride have been developed, and these are presented in Table II.

Geilmann, Wrigge, and Blitz(6) gave the first report of the preparation and characterization of rhenium(V) chloride. This paper seemed to settle most of the disputes concerning the reaction products of rhenium and chlorine. Geilmann and Wrigge (7) followed with a number of reactions of both rhenium(V) chloride and rhenium(III) chloride with water, oxygen, hydrogen, alkali, and acid. See Table III.

Table I. Early Reactions of Rhenium and Chlorine.

Reaction	Date	Ref.
1. $Re + Cl_2 \longrightarrow ReCl_6$	1928	8
2. $Re + Cl_2 \longrightarrow ReCl_6$ (brown) + $ReCl_7$ (grass-green)	1929	9
3. $Re + Cl_2 \longrightarrow ReCl_6$ (Temp. at 500°C)	1931	10
$Re + Cl_2 \longrightarrow ReCl_7$ (With light heating)		
$ReCl_7 \longrightarrow ReCl_6$ (Temp. at 500°C)		
4. $Re + Cl_2 \longrightarrow ReCl_4$ (Black needles with a trace of brown compound)	1931	11
$Re + HCl \longrightarrow$ No Reaction up to 900°C		
5. $Re + Cl_2 \longrightarrow ReCl_{4.3}$	1931	12
$ReCl_{4.3} \longrightarrow$ less volatile product (heated in a stream of dry nitrogen)		
$ReCl_{4.3} + Cl_2 \longrightarrow ReCl_{4.3}$ (Heated in a steam of chlorine gave complete volatilization).		
6. $Re + O_2 + Cl_2 \longrightarrow ReO_2Cl_3$ (This is the brown compound in Ref. 11).	1932	13
7. $Re + Cl_2 \longrightarrow ReCl_4$ (Temp. at 650°C)	1932	14
8. $Re + Cl_2 \longrightarrow ReCl_3 + ReCl_4$	1932	15
9. First prepared and characterized what are now regarded as the only two authentic oxychlorides of rhenium; $ReOCl_4$ and ReO_3Cl.	1932	16

Table I. (Continued)

Reaction	Date	Ref.
10. $Re + Cl_2 \longrightarrow ReCl_5$ (Some $ReCl_3$ left over after vacuum sublimation of the $ReCl_5$).	1933	6
11. Claims the $ReCl_3$ of Ref. 15 is Re^{IV} and may be Re_2Cl_6O.	1934	17
12. Declares Ref. 17 to be wrong - $ReCl_3$ of Ref. 15 is $ReCl_3$.	1934	18
13. $Re + Cl_2 \longrightarrow ReCl_5$ (The "standard" preparation).	1939	19

Table II. Representative Preparations of Rhenium(V) Chloride.

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1. $2Re + 5Cl_2 \longrightarrow 2ReCl_5$

   Done in an all-glass reactor with the strict exclusion of water and oxygen. Ref., Geilmann, et al.(6) and Hurd and Brimm (19).

2. $Re_2O_7 + 7CCl_4 \longrightarrow 2ReCl_5 + 7COCl_2 + 2Cl_2$.

   Done in a high pressure bomb. Ref., Knox, et al.(20).

3. $Re_2S_7 \longrightarrow Re_2S_3Cl_4$

   This step done using a 1:5 mixture of chlorine-carbon dioxide at a temperature of 120°C.
   $Re_2S_3Cl_4 \longrightarrow ReSCl_2$. This step done using chlorine and a temperature of 400-500°C.
   $ReSCl_2 \longrightarrow ReCl_4 \longrightarrow ReCl_5$. This step done at 450-500°C, in chlorine. Ref., Glukhov, et al. (21).

4. $Re_2S_7 + CCl_4 \longrightarrow ReCl_5$

   Done in a high pressure bomb. Ref., Bordawil, et al. (22).

5. $4KReO_4 + 16CCl_4 \longrightarrow 2ReCl_5 + 2K_2ReCl_6 + 5Cl_2 + 16COCl_2$

   Done in a high pressure bomb. Ref., Horner et al. (23).

Table III. Reactions of Rhenium(V) Chloride.

1. $8ReCl_5 + 7O_2 \longrightarrow 5ReOCl_4 + 3ReO_3Cl + 17Cl$

   These were run at 200°C. The $ReOCl_4$ was a brown mass of thick needles, M.P. 29.5-30.5°C. The ReO_3Cl was a volatile, light green liquid which, in a cold bath, turned to white needles, M.P. 3-4°C. No evidence for ReO_2Cl_3, see Ref. (13), could be found.

2. $ReCl_5 + 2KCl \longrightarrow K_2ReCl_6 + 1/2Cl_2$

3. $3ReCl_5 + 16NaOH \longrightarrow 2ReO\cdot XH_2O + NaReO_4 + 15NaCl + 8H_2O$

   This is a disproportionation reaction:
   $3Re^{V} \longrightarrow 2Re^{IV} + Re^{VII}$.

4. $ReCl_5 + \text{acid} \longrightarrow HReO_4 + H_2ReCl_6 + Cl_2$

   This was done using hydrochloric acid, of a concentration ranging between 2 and 18% HCl.

5. $2Ag_2ReCl_6 \longrightarrow 4AgCl + ReCl_3 + ReCl_5$

   This was done by heating the silver hexachlororhenium(IV) to about 400°C in a vacuum. No evidence for rhenium(IV) chloride could be found.

6. $ReCl_5 \longrightarrow ReCl_3 + Cl_2$

   This was done by heating the rhenium(V) chloride in a stream of dry nitrogen.

Prior to 1968, little was known regarding the structure of rhenium(V) chloride. Magnetic measurements had led to speculation that rhenium(V) chloride possessed a trimeric structure, $[Re_3Cl_{12}]\ Cl_3$, similar to rhenium(III) chloride, $(Re_3Cl_{12})^{3-}$ (24). Mucher, et al. (25), in 1968, resolved the structure of rhenium(V) chloride by x-ray analysis and found it to be dimeric, composed of two octahedra with a common edge. See Figure 1.

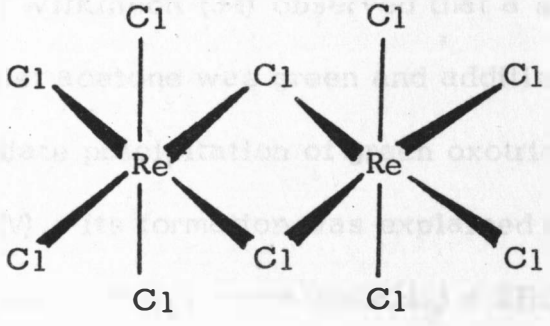


Figure 1. Rhenium(V) Chloride.

Rhenium(V) chloride has been used as the reactant for the formation of a number of interesting compounds. Because of their unusual nature, these are given in Table IV.

In 1964 Johnson, Lock and Wilkinson (33) made the first attempt to react rhenium(V) chloride with group VA ligands. They obtained green, polymeric tetrachlorotriphenylphosphinerhenium(IV), $[ReCl_4(C_6H_5)_3P]_n$, from the reaction of rhenium(V) chloride and triphenylphosphine in dry acetone.

Grove and Wilkinson (34) observed that a solution of rhenium(V) chloride in moist acetone was green and addition of triphenylphosphine gave an immediate precipitation of green oxotrichlorobis(triphenylphosphine)rhenium(V). Its formation was explained as follows:

$$ReCl_5 + H_2O \longrightarrow (ReOCl_3) + 2HCl$$

$$(ReOCl_3) + 2PPh_3 \longrightarrow ReOCl_3(PPh_3)_2$$

where PPh_3 = triphenylphosphine.

The presence of the intermediate, $ReOCl_3$, although not isolated, was rationalized by the green color of the solution and the formulation of the product.

The reaction of rhenium(V) chloride and pyridine in moist acetone gave a green precipitate which was not characterized (33). Concentration of the mother liquor yielded red-orange crystals of dioxotetrakis(pyridine)rhenium(V) chloride dihydrate, $ReO_2Py_4\ Cl\cdot 2H_2O$, where

Table IV. Representative Products from Reactions of Rhenium(V) Chloride.

1. Bis(benzene)rhenium(I) tetrachloroaluminate(III) $(C_6H_6)_2ReAlCl_4$ (26).

2. Bis(cyclopentadienyl)rhenium(I)hydride $(C_5H_5)_2ReH$ (27).

3. Trichlorodiacetatorhenium(V) $[ReCl_3(CH_3COO)_2]_n$ (28).

4. Tris(cis-1,2-diphenyllene-1,2-dithiolato)rhenium $Re[(S_2C_2(C_6H_5)_2]_3$ (29).

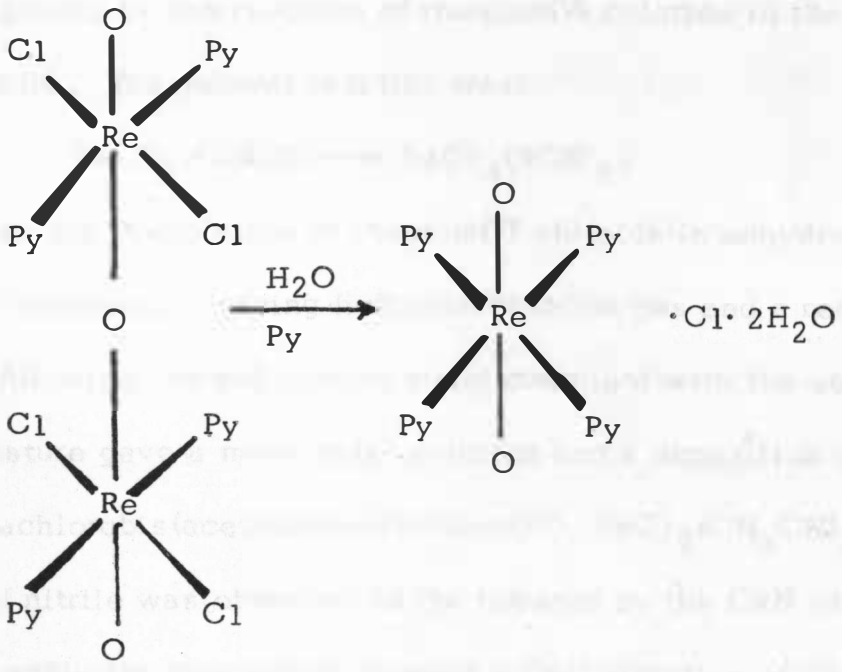
5. Chloropentakis(trifluorophosphine)rhenium(I) $ClRe(PF_3)_5$ (30).

6. Cesium hexathiocyanatorhenate(I) $CsRe(SCN)_6$ (31).

7. Benzenecyclopentadienylrhenium(I) $C_5H_5ReC_6H_6$ (32).

Py = pyridine. The compound could also be prepared by refluxing oxotrichlorobis(triphenylphosphine)rhenium(V) and pyridine in ethanol. Later, Johnson, Taha, and Wilkinson (35) reported the formulation of the green compound as μ-oxodioxtetrachlorotetrakis(pyridine)dirhenium-(V), $Re_2O_3(Py)_4Cl_4$, and showed that it was an intermediate in the conversion of oxotrichlorobis(triphenylphosphine)rhenium(V) to dioxotetrakis-(pyridine)rhenium(V) chloride. The following reaction is given to illustrate the overall reaction scheme:

$$2ReCl_5 + 3H_2O + 10Py \longrightarrow$$



Cotton, Robinson, and Walton (36) reported that attempts to repeat the reaction resulted in the formation of a dark green powder and a violet solution. Since the green powder possessed solubilities different from those reported by Johnson, it could not be μ-oxodioxotetrachlorotetrakis(pyridine)dirhenium(V), but they made no further efforts to characterize the green solid. They did find that aged rhenium(V) chloride gave a mixture of red and green crystals that could be separated by hand and had the characteristics of the compounds formulated by Johnson.

Rouschias and Wilkinson (37) prepared a series of rhenium-nitrile complexes by the reaction of rhenium(V) chloride in the corresponding nitrile. The general reaction was:

$$ReCl_5 + 2RCN \longrightarrow ReCl_4(RCN)_2.$$

For example, the dissolution of rhenium(V) chloride in anhydrous acetonitrile was exothermic, giving hydrogen chloride gas and a red-brown solution. Allowing the solution to stand overnight with the strict exclusion of moisture gave a much paler solution and a deposition of green-yellow tetrachlorobis(acetonitrile)rhenium(IV), $ReCl_4(CH_3CN)_2$. The coordinated nitrile was observed in the infrared by the C≡N vibration at 2292 cm^{-1} while the free nitrile showed a C≡N vibration at 2247 cm^{-1}. The authors found that the acetonitrile complex reacted readily in acetonitrile with triphenylphosphine to form red tetrachlorobis-

(triphenylphosphine)rhenium(IV), $ReCl_4(PPh_3)_2$.

Very recently, Allen, et al. (38) demonstrated that the purple nonachlorodirhenium(III-IV), $Re_2Cl_9^{2-}$, species was obtained from rhenium(V) chloride in a solution of acetone and water. Such a solution, when treated with a solution of tetraphenylarsonium hydrogen dichloride in chloroform first turned green and then purple and finally yielded purple bis(tetraphenylarsonium) nonachlorodirhenate(III-IV) and colorless tetraphenylarsonium perrhenate, by the reaction:

$$7ReCl_5 + 12H_2O = 2Re_2Cl_9^{2-} + 3ReO_4^{1-} + 17HCl + 7H^+.$$

Of considerable importance to the work presented herein is the propensity of rhenium to form dinuclear species containing strong rhenium to rhenium bonds. The first to realize this was Cotton, who presented a series of papers in 1965 (39), (40), (41) elucidating the nature of the octachlorodirhenate(III), $Re_2Cl_8^{2-}$, ion. It was determined that this ion had a very short rhenium-rhenium distance with a quadruple bond, and an eclipsed configuration. See Figure 2.

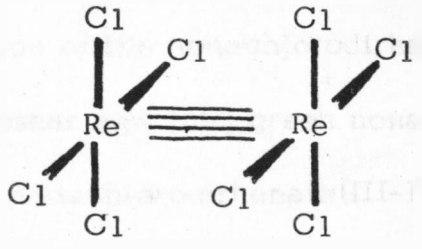


Figure 2. Structure of Octachlorodirhenate(III) Ion.

The stability of the rhenium-rhenium bond towards oxygen and sulfur ligands was investigated by Cotton, Oldham, and Walton (42).

In 1967 Cotton, Robinson, and Walton (36) published a report on the chemistry of rhenium(IV) chloride, which they had received by accident and whose synthesis they could not duplicate. They distinguished this crystalline form from a more amorphous form of rhenium(IV) chloride prepared in 1964 by Brown and Colton (43) by calling Brown and Colton's material α-rhenium(IV) chloride and their own, β-rhenium(IV) chloride. Cotton reported that, under the proper conditions, either the octachlorodirhenate(III) ion or a new species, nonachlorodirhenate(III-IV), $Re_2Cl_9^{2-}$, could be obtained from the rhenium(IV) chloride. The fact that the nonachlorodirhenate(III-IV) ion could be readily converted to octachlorodirhenate(III) led Cotton to speculate that the two possessed the same basic structure, with the nonachlorodirhenate(III-IV) species having an axial chlorine atom. This view was supported by the magnetic moment of the compound.

Soon thereafter, Bonati and Cotton (44) published a more complete investigation of the nonachlorodirhenium(III-IV) species and brought forth another new ion, green nonachlorodirhenate(IV), $Re_2Cl_9^{1-}$. The nonachlorodirhenate(III-IV) was found to be much more stable in solution than the nonachlorodirhenate(IV). They summarized their reactions with the flow sheet given in Figure 3.

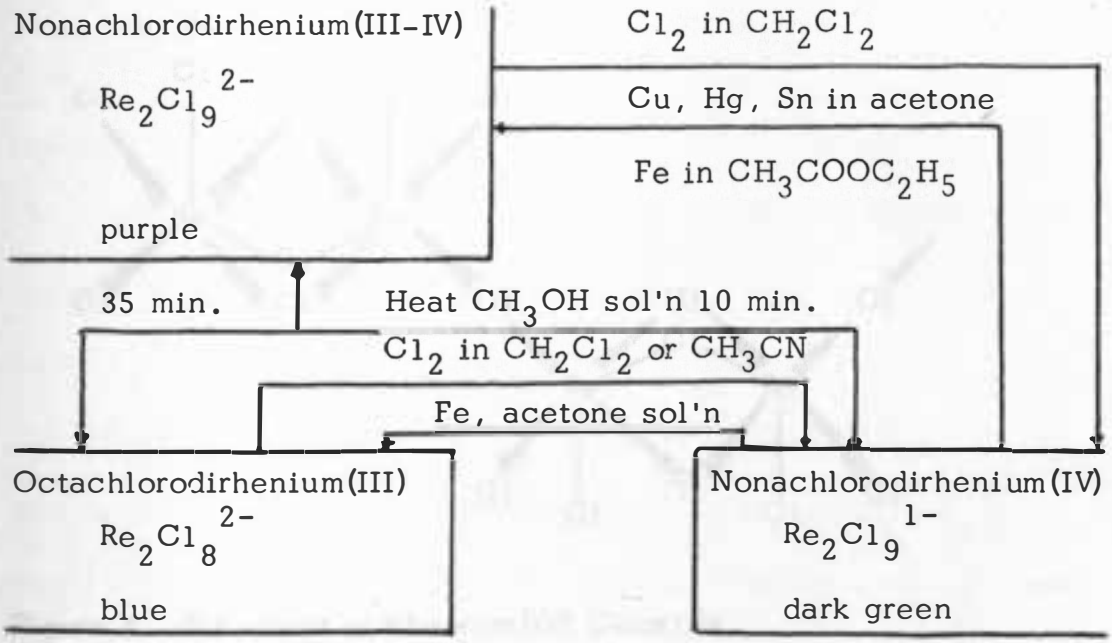


Figure 3. A flow sheet summarizing the interconversion of the various $Re_2Cl_8^{2-}$, $Re_2Cl_9^{1-}$, and $Re_2Cl_9^{2-}$ species.

The nonachlorodirhenate(III-IV) had one strong infrared absorption in the region for a rhenium-chlorine stretching frequency (321 cm^{-1}) while the nonachlorodirhenate(IV) had two such absorptions, at 353 cm^{-1} and 250 cm^{-1}. This suggested that perhaps the nonachlorodirhenate(III-IV) had the structure previously discussed while the nonachlorodirhenate(IV) could have a structure like β-rhenium(IV) chloride. Bennett, et al. (45) determined that the β-rhenium(IV) chloride was composed of Re_2Cl_9 units strung together by sharing of terminal chlorine atoms. See Figure 4.

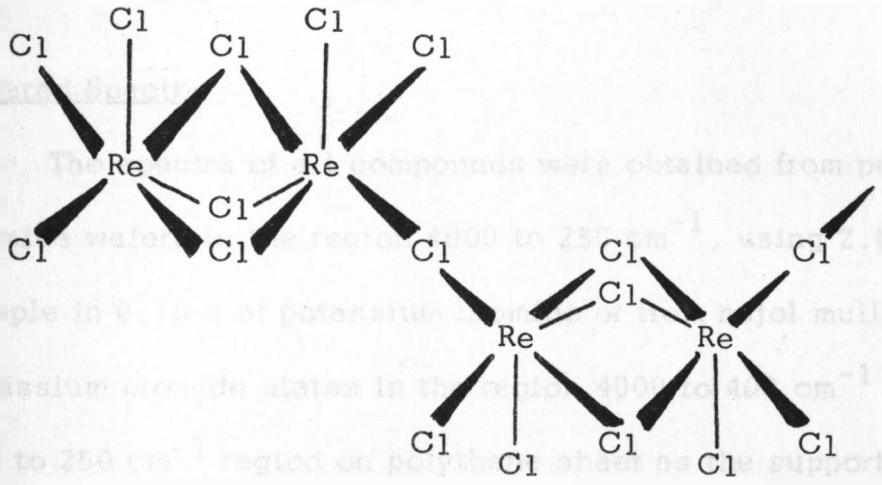


Figure 4. Structure of Rhenium(IV) Chloride.

EXPERIMENTAL SECTION

Infrared Spectra

The spectra of all compounds were obtained from potassium bromide wafers in the region 4000 to 250 cm^{-1}, using 2.0 mg of sample in 0.10 g of potassium bromide or from nujol mulls on potassium bromide plates in the region 4000 to 400 cm^{-1} and the 400 to 250 cm^{-1} region on polythene sheet as the support. The spectra were obtained on a model 521 Perkin-Elmer grating spectrophotometer. Using the 2X or 5X abcissa expansion from 400 to 250 cm^{-1}, the time of scan was slowed to eighty minutes. Other settings were: split program, in-1000; gain 5; attenuator speed, 1100; suppression, 6; source current, 0.8 amps. Preliminary infrared spectra were done on a Beckman IR-5, equipped with sodium chloride optics, using nujol mulls on sodium chloride plates in the region 4000 to 650 cm^{-1}.

Electronic Spectra

The electronic spectra were obtained in solution on either a Beckman DK-2A or a Beckman DB spectrophotometer using one centimeter silica cells.

Molecular Weights

The molecular weights were determined on a Mechrolab 301A vapor pressure osmometer, operating at an ambient temperature of 37°C.

Conductivities

The conductivities were done at room temperature, using an Industrial Instruments Conductivity Bridge, model RC16B2, operating at either 60 or 1000 Hz. The cell was a standard platinum electrode cell, with the cell constant calculated using potassium chloride.

Nuclear Magnetic Resonance Spectra

The nuclear magnetic resonance (nmr) spectra were obtained on a Varian A-60-A spectrometer, operating at room temperature.

Triphenylphosphine

The triphenylphosphine was obtained from Alpha Inorganics, Inc. and was used as received.

Potassium Perrhenate

The potassium perrhenate was used as received from the S.W. Shattuck Chemical Company.

Triphenylphosphine Oxide

The triphenylphosphine oxide was obtained from M & T, Inc., and was used without further purification.

Dichloromethane

The dichloromethane was obtained from Fisher Scientific Company and was used as received. When required, it was dried by the method of Bagnall, Brown, and duPreez (46).

Chloroform

The chloroform was obtained from Mallinckrodt Chemical Works and was used without further purification.

Acetone

The acetone was obtained from Worum Chemical Company. The acetone was dried over anhydrous calcium chloride for one day and then carefully distilled onto Linde 4A molecular sieves. The acetone was allowed to stand over the sieves two to five days prior to use. All distillations were carried out on a three-foot glass column and under nitrogen which had been dried by passage through a tube containing a calcium chloride-phosphorous pentoxide mixture.

Rhenium Pentachloride

Rhenium pentachloride was prepared by the method of Gehrke (47).

Rhenium Metal

The rhenium metal was obtained from Cleveland Refractory Metals Company and was used as received.

Pyridine

The pyridine was obtained from Eastman Organic Chemical Company. It was dried by distillation from anhydrous calcium chloride onto Linde 4A molecular sieves where it was stored for three days prior to use.

Aluminum Oxide

The rhenium compounds discussed in this paper were found to decompose upon chromatography columns of other than acidic aluminum oxide (alumina). The basic aluminum oxide obtained from J. T. Baker Chemical Company was washed three times with 12N hydrochloric acid and seven times with water. It was dried at 260°C for four days.

Tetraphenylarsonium Chloride

The tetraphenylarsonium chloride was used as received from Eastman Organic Chemical Company.

Hypophosphorous Acid

The hypophosphorous acid (50%) was obtained from the Fisher Scientific Company and used without further purification.

Mesityl Oxide

The mesityl oxide was obtained from Eastman Organic Chemical Company. It was distilled onto Linde 4A molecular sieves the day of the reaction, and distilled from the molecular sieves with the fraction boiling at 126-127°C used.

Acetonitrile

The acetonitrile was obtained from Eastman Organic Chemical Company. When used as a conductivity and molecular weight solvent, it was dried over anhydrous calcium chloride and distilled onto phosphorous pentoxide. It was then distilled onto Linde 4A molecular sieves where it was stored. When needed, the acetonitrile was distilled off the molecular sieves into a clean, dry flask.

Diethyl Ether

The diethyl ether was used as received from Fisher Scientific Company for purposes of inducing crystallization. For the preparation of the phosphonium salts (given later), the ether was dried over anyhdrous calcium chloride, and distilled from the calcium chloride onto sodium hydride. The ether was then distilled into a clean, dry flask.

Phosphorous Pentoxide

The phosphorous pentoxide was used as received from the J. T. Baker Chemical Company.

Hydrogen Chloride

The hydrogen chloride was generated by the action of 36N sulfuric acid on sodium chloride. It was dried by passage through a calcium chloride tube.

Benzene

Benzene was obtained from Fisher Scientific Company and dried by distillation from sodium ribbon onto fresh sodium ribbon. It was distilled into a clean, dry flask immediately prior to use.

1,2,3,4-Tetrahydronapthalene

The 1,2,3,4-tetrahydronapthalene was used as received from Eastman Organic Chemical Company.

Hydrogen Bromide

The hydrogen bromide was prepared by dropping liquid bromine onto 1,2,3,4-tetrahydronapthalene in the presence of powdered iron. Bromine vapor was removed by passing the hydrogen bromide through red phosphorous.

Diethylphenylphosphine

The diethylphenylphosphine was prepared by the method of Mann and Chaplin (48).

Tetraphenylphosphonium Chloride

The tetraphenylphosphonium chloride was prepared by the method of Horner, et al. (49).

Bis(tetraethylammonium) Hexachlorhenate(IV).

The bis(tetraethylammonium) hexachlorhenate(IV) was prepared by the method of Chatt, et al. (50).

Bis(p-toluidinium) Hexachlororhenate(IV).

The bis(p-toluidinium) hexachlororhenate(IV) was prepared by the method of Adrian and Margulis (51).

Bis(pyridinium) Hexachlororhenate(IV).

Bis(pyridinium) hexachlororhenate(IV) was prepared by the method of Adrian and Margulis (51).

Bis(diethylammonium) Hexachlororhenate(IV).

Bis(diethylammonium) hexachlororhenate(IV) was prepared by the method of Adrian and Margulis (51).

Bis(diethylphenylphosphonium) Hexachlororhenate(IV).

Bis(diethylphenylphosphonium) hexachlororhenate(IV) was prepared by the method of Chatt, et al. (52).

Analyses.

The carbon and hydrogen analyses were performed by the analysts at South Dakota State University, Galbraith Laboratories in Knoxville, Tennessee, and Schwarzkopf Laboratory in Woodside, New York. Rhenium was determined quantitatively by the spectrophotometric method of Meloche, Martin, and Webb (53). Chlorine was determined by the gravimetric method of Beamish (54).

Preliminary Remarks Regarding Experimental Conditions.

The reactions of the rhenium(V) chloride were carried out in a Hamilton dry box, unless otherwise mentioned. The atmosphere in the box was nitrogen, which had been passed through a tube containing copper turnings at 350°C to remove any oxygen and then through a tube containing a calcium chloride-phosphorous pentoxide mixture to remove traces of moisture. To maintain a low moisture content in the dry box, four petri dishes containing phosphorous pentoxide were kept in the dry box. As a crust of hydrated phosphorous pentoxide was formed on the surface of the dishes, it was scraped off, exposing fresh phosphorous pentoxide to renew its water-remving capabilities.

All reagents used for the reactions of rhenium(V) chloride were carefully dried prior to admission to the dry box unless otherwise noted.

The freshly prepared rhenium(V) chloride was handled in the dry box to minimize hydrolysis of the product. The tube containing the rhenium(V) chloride was opened using a device especially designed to open a sealed glass tube in the dry box without shattering the tube and contaminating the product with glass fragments. The device consisted of a metal pan (approximately 15 cm in diameter and 10 cm deep) containing sufficient sand to fill the pan. In the center of the

pan was an asbestos plug with the center hollowed out. This plug was made by pouring a water suspension of shredded asbestos onto a plastic Buchner funnel 6 cm in diameter and 4 cm deep, using a water pump for suction. A size 00 crucible was placed in the center of the Buchner funnel and when the asbestos had filled the funnel and suction pulled on it sufficiently to pack the asbestos, the suction was removed and the crucible removed, leaving the necessary hole in the center of the asbestos plug. The entire plug was carefully removed from the Buchner funnel and wrapped carefully with wet asbestos tape to provide additional strength to the plug. The entire plug was then placed in the center of the pan and the sand was used to fill the rest of the pan. In the center of the plug was placed a coil of asbestos-covered nichrome wire, coiled so that both ends could be connected to a length of ordinary zipper cord wich was terminated by a standard 110 volt two-prong plug.

The device was operated by plugging into a Variac with a setting of about 15 volts on the Variac. As soon as the coil glowed the end of a length of Pyrex cane was introduced into the center of the coil, melting the end of the cane and this end was placed on the end of a scratch which had been previously made in the tube to be opened. This treatment caused the tube to crack such that it could be opened

without splintering the glass.

The rhenium(V) chloride was removed from the tube and quickly placed in previously dried (110°C, overnight), tared screw-capped vials. These were sealed, removed from the dry box, weighed, and returned to the dry box for storage until use.

Reaction of Rhenium(V) Chloride and Triphenylphosphine in Acetone.

Rhenium(V) chloride (1.29 g, 3.56 mmoles) was dissolved in 25 ml of acetone. The solution was initially red-brown but as more rhenium(V) chloride dissolved a green coloration appeared in the solution. A solution of triphenylphosphine (3.893 g, 14.9 mmoles) in 10 ml of acetone was added, immediately causing the solution to turn green. Green crystals soon appeared at the bottom of the flask. In about thirty minutes the solution had turned red-brown and after four hours the crystals were brown.

After standing, capped, overnight in the dry box, dark red crystals were filtered on scintered glass from a red-purple solution, washed with two 5 ml portions of acetone, and removed from the dry box.

The red crystals were purified by stirring in chloroform until most were dissolved. The deep red solution was then filtered from a small amount of undissolved material and the filtrate passed down a 25 cm column of alumina. This gave a red fraction and a small yellow

fraction as well as a dark ring of decomposed material left at the top of the column. The yellow fraction was combined with those from the mother liquor (see following). The red fraction was concentrated on a rotary evaporator until crystallization started and then allowed to stand overnight, giving 0.758 g (25.2%) of red tetrachlorobis(triphenylphosphine)rhenium(IV). Consult the Appendix for the infrared spectrum of the compound.

Anal. Calcd. for $C_{36}H_{30}P_2ReCl_4$: C, 50.76; H, 3.53. Found: C, 50.08; H, 3.75.

The mother liquor was passed down a column of alumina giving, in order of appearance at the bottom of the column, pink, yellow, and purple bands. The purple material failed to elute completely from the column using acetone but acetonitrile did effect a removal of the compound. Remaining on the column was a blue compound, which could not be removed, even with the use of a number of different solvents, such as methylene chloride, methanol, benzene, diethyl ether, and N,N-dimethylformamide. Heating in any of those solvents caused the color to turn from blue to gray.

The fractions were collected separately by color and concentrated to approximately one-third their volumes on a rotary evaporator. Diethyl ether was added to induce crystallization and the crystals

were collected on scintered glass, washed with ether, and dried at 1 mm Hg and 80°C.

This procedure gave 0.436 g (12.6%) of yellow 1,1-dimethyl 3-oxobutyltriphenylphosphonium pentachlorotriphenylphosphinerhenate(IV). Consult the Appendix for the infrared, nmr and electronic spectra, and the x-ray powder pattern.

Anal. Calcd. for $C_{42}H_{41}P_2ReOCl_5$: C, 51.10; H, 4.20; Re, 18.90; Cl, 17.99; mol wt, 987. Found: C, 50.78; H, 4.31; Re, 19.67; Cl, 17.00; mol wt, 1083; molar conductivity, 16.9 ohm^{-1} cm^2 (nitrobenzene).

Also obtained was 0.012 g of a purple mixture of bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium)nonachlorodirhenate(III-IV) and bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) octachlorodirhenate(III). Consult the Appendix for the infrared and electronic spectra and the x-ray powder pattern.

Anal. Calcd. for $C_{48}H_{52}O_2P_2Re_2Cl_9$: C, 40.76; H, 3.71; Re, 26.3. Calcd. for $C_{48}H_{52}O_2P_2Re_2Cl_8$: C, 41.81; H, 3.80; Re, 27.0. Found: C, 41.04; H, 3.77; Re, 26.17; molar conductivity, 258 ohm^{-1} cm^2.

The weights of the products represented approximately 50% of the rhenium. The rest of the rhenium was lost on the chromatography column, and in the filtrates from the final crystal growths.

The variously colored fractions rarely separated completely from each other on the column, and rather than go through the time consuming process of continually reapplying the mixtures to the chromatography column, the tails of the bands were set aside.

Reaction of Rhenium(V) Chloride and Triphenylphosphine in Acetone with Water Added.

Rhenium(V) chloride (1.159 g, 1.18 mmoles) was dissolved in 25 ml of acetone, giving a dark red solution with a tinge of green. To this solution was added three drops of water, which had been carefully distilled after refluxing under nitrogen for one-half hour. This seemed to cause the solution to turn more green. To the resulting solution was added a solution of triphenylphosphine (3.337 g, 12.7 mmoles) in 10 ml of acetone containing two drops of water. From the resulting green solution were deposited green crystals. After standing, capped, for one hour, 0.90 g of green oxotrichlorobis-(triphenylphosphine) rhenium(V) was collected on sintered glass, washed with acetone, and recrystallized from methylene chlroide, giving 0.75 g (28.2%) of product. Consult the Appendix for the infrared spectrum.

Anal. Calcd. for $C_{36}H_{30}P_2ReOCl_3$: C, 51.99; H, 3.61; Re, 22.8; Cl, 13.1. Found: C, 51.80; H, 3.82; Re, 23.64; Cl, 13.27.

The purple filtrate was chromatographed through alumina giving red, yellow, and purple fractions. These were worked up as before, giving 0.0166 g (0.62%) of red tetrachlorobis(triphenylphosphine)-rhenium(IV), 0.401 g (13.15%) of yellow 1,1-dimethyl-3-oxobutyl-triphenylphosphonium pentachlorotriphenylphosphinerhenate(IV) and 0.030 g of the purple mixture of bis(1,1-dimethyl-3-oxobutyltri-phenylphosphonium) octachlorodirhenate(III) and bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) nonachlorodirhenate(III-IV). These were characterized by their infrared and electronic spectra.

The Reaction of "Aged" Rhenium(V) Pentachloride with Triphenyl-phosphine in Acetone.

Rhenium(V) chloride (1.3533 g, 3.68 mmoles) was "aged" by allowing it to stand, uncapped, in the dry box for two days prior to use and was then dissolved in 25 ml of acetone, giving a dark red-brown solution. To this was added a solution of triphenylphosphine (4.000 g, 16.30 mmoles) in 10 ml of acetone. Within a minute green crystals were seen to have precipitated from a green solution. After standing, capped, overnight in the dry box, brown crystals were collected on scintered glass.

The brown solid was stirred with chloroform and red-green crystals were filtered from the resulting deep red solution after stirring for fifteen minutes. These crystals were stirred in more chloroform and, after repeating the process several times, there was left only a red chloroform solution and green crystals of oxotrichlorobis(triphenylphosphine)rhenium(V).

The red chloroform solutions were combined and reduced to one-third their original volume before passing them down a column of alumina. There was left on the column a small, dark band at the top of the column, attributed to a small amount of oxotrichlorobis-(triphenylphosphine)rhenium(V) which did dissolve in the chloroform but decomposed upon the column. The red solution was collected and set aside.

The original filtrate, purple in color, concentrated slightly on a rotary evaporator, was passed down a column of alumina and split into yellow and purple bands, in order of appearance at the bottom of the column. The purple again could not be completely eluted using acetone but was removed using acetonitrile. The alumina had a blue coloration which remained. The fractions were worked up as previously described, giving 0.382 g (10.6%) of yellow 1,1-dimethyl-3-oxobutyltriphenylphosphonium pentachlorotriphenylphosphinerhenate(IV) and 0.052 g of the purple mixture of

bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) nonachlorodirhenate(III-IV) and bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) octachlorodirhenate(III). The compounds were characterized by their infrared and electronic spectra.

Rhenium(V) Chloride and Triphenylphosphine in Anhydrous Acetone with Immediate Collection of Initial Green Product.

The reaction was run in order to establish the identity of the original green precipitate from the rhenium(V) chloride-triphenylphosphine reaction. Rhenium(V) chloride (0.4134 g, 1.13 mmoles) was dissolved in 25 ml of acetone. To this solution was added a solution of triphenylphosphine (1.1570 g, 4.4 mmoles) in 10 ml of acetone. Green crystals came down rapidly from a green solution. These crystals (0.1010 g, 10.8%) were filtered from the solution approximately five minutes after the time that the triphenylphosphine was added to the rhenium(V) chloride. The infrared spectrum of the green crystals indicated that they were oxotrichlorobis(triphenylphosphine)rhenium(V).

The rest of the reaction proceeded as described previously, with the isolation of red tetrachlorobis(triphenylphosphine)rhenium(IV), yellow 1,1-dimethyl-3-oxobutyltriphenylphosphonium pentachlorotriphenylphosphinerhenate(IV), and the purple mixture of

bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) nonachlorodirhenate(III-IV) and bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) octachlorodirhenate(III). These were characterized by their infrared spectra.

The Reaction of Rhenium(V) Chloride and Triphenylphosphine in Moist Acetone with Subsequent Addition of Diethyl Ether.

Rhenium(V) chloride (0.6565 g, 1.80 mmoles) was dissolved in 15 ml of acetone in the dry box. The acetone was stock, technical grade and was used without further purification. The solution was removed from the dry box and triphenylphosphine (0.970 g, 3.70 mmoles) dissolved in 8 ml of stock acetone was added. The resulting green solution was stirred in the open air for one and three-fourths hours. At the end of that time 0.61 g (40.6%) of greenish-yellow oxotrichlorobis(triphenylphosphine)rhenium(V), as identified by its infrared spectrum, was collected by filtration. It was washed with ether and dried at 1 mm Hg and 20°C.

To the purple mother liquor was added 40 ml of diethyl ether, precipitating a purple oil. This was dissolved in 5 ml of acetone and 40 ml of ether was added. The solution was allowed to stand, capped, overnight. The next day a small amount (4 mg) of yellow 1,1-dimethyl-3-oxobutyltriphenylphosphonium

pentachlorotriphenylphosphinerhenate(IV) (from its infrared spectrum) had separated from the purple crystals. The purple crystals (0.25 g) were collected by filtration and dried by vacuum (1.0 mm Hg) and 25°C.

A small portion of these crystals was dissolved in acetone and chromatographed on a column of alumina, splitting cleanly into yellow and purple bands. The purple band was again eluted with the aid of acetonitrile and was crystallized by concentration of the fraction on a rotary evaporator (no heat applied) and adding ether. The infrared spectrum indicated that the crystals obtained were the purple mixture of bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) nonachlorodirhenate(III-IV) and bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) octachlorodirhenate(III). Similar treatment of the yellow fraction gave yellow crystals whose infrared spectrum was identical to that of 1,1-dimethyl-3-oxobutyltriphenylphosphonium pentachlorotriphenylphosphinerhenate(IV).

A portion of the purple crystals from the original reaction (0.05 g) was pumped at 80°C and 1 mm Hg. In about twenty minutes the crystals had expanded considerably in volume while remaining purple in color. There were 0.05 g of these recovered. A small portion of this material was dissolved in acetone and passed

down a short column of alumina, again giving yellow and purple bands.

Attempted Conversion of Bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) Nonachlorodirhenate(III-IV) to 1,1-Dimethyl-3-oxobutyltriphenylphosphonium Nonachlorodirhenate(IV).

The purple mixture of bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) nonachlorodirhenate(III-IV) and bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) octachlorodirhenate(III) was dissolved in methylene chloride and chlorine gas bubbled through the solution. The color of the solution, in all attempts, turned green immediately. The solvent was removed on a rotary evaporator and the green oily residue twice extracted with ether. The residue was then crystallized at 0.5 mm Hg and room temperature. In all but one case the green residue turned purple during the attempts to crystallize it. Ethyl acetate, carbon tetrachloride, hexane, and chloroform were also tried with the same results. Immediate precipitation by addition of hexane gave a green tar which turned purple upon attempted crystallization. In one attempt, hexane was added to the green methylene chloride solution while the chlorine gas was still bubbling through the solution. This gave precipitate of green tar which again turned purple upon attempts to crystallize it.

In one attempt, using the method first outlined, green crystals

were obtained. The infrared spectrum of the product indicated that it was 1,1-dimethyl-3-oxobutyltriphenylphosphonium nonachlorodirhenate-(IV), and that some decomposition of the cation had occurred. Returning to the product one day later, it was discovered that it had turned purple.

The Reaction of Rhenium(V) Chloride and Pyridine in Acetone.

Rhenium(V) chloride (1.325 g, 3.65 mmoles) was dissolved in 25 ml of acetone and to this was added 11 ml of pyridine. The solution was a very dark brown, with no observable crystal deposition. After allowing the solution to stand, capped, for two days in the dry box, 0.20 g (11.7%) of red-orange crystals were collected on sintered glass and washed with acetone. The filtrate was concentrated to one-half its original volume and allowed to stand six hours. It was filtered through sintered glass, giving 0.18 g (10.5%) more of the red-orange dioxotetrakis(pyridine)rhenium(IV) chloride dihydrate. Consult the Appendix for the infrared spectrum.

Anal. Calcd. for $C_{20}H_{24}N_4O_4ReCl$: C, 39.62; H, 3.97.

Found: C, 39.11; H, 3.88.

The Reaction of Rhenium(V) Chloride and Triphenylphosphine Oxide in Acetone.

Rhenium(V) chloride (0.6552 g, 1.80 mmoles) was dissolved in 25 ml of acetone giving a brown solution with a tinge of green. To this was added triphenylphosphine oxide (2.3762 g, 8.52 mmoles) in 15 ml of acetone. The dark solution was allowed to stand, capped, for two days, in the dry box and at that time was filtered through sintered glass. A yield of 0.721 g of purple bis[μ-hydrogen-bis(triphenylphosphine oxide)] nonachlorodirhenate(III-IV) was collected and washed with ether. It was recrystallized from acetone-ether. Consult the Appendix for the infrared and electronic spectra.

Anal. Calcd. for $C_{72}H_{62}O_4P_4Re_2Cl_9$: C, 47.87; H, 3.46; Cl, 17.66. Found: C, 48.14; H, 3.62; Cl,16.93.

molar conductivity, 258 ohm^{-1} cm^2.

Bis(1,1-dimethyl-3-oxobutyl(triphenylphosphonium) Octachloro-dirhenate(III).

Bis(tetra-n-butylammonium) octachlorodirhenate(III) (0.5 g, 0.44 mmoles) was dissolved in a minimum volume of methylene chloride (ca. 35 ml). To this was added a solution of 1,1-dimethyl-3-oxobutyltriphenylphosphonium hydrogen dichloride (0.75 g, 1.73 mmoles) in 25 ml of ethanol. The resulting solution was allowed to air evaporate to about 20 ml and 0.45 g (75.0%) of blue-green crystals

of product were collected on scintered glass. They were washed with two 10 ml portions of ether and dried by suction on the sintered glass. They were recrystallized from methylene chloride-ether.

Anal. Calcd. for $C_{48}H_{52}P_2O_2Re_2Cl_8$: C, 41.81; H, 3.80; mol wt, 1378. Found: C, 41.20; H, 3.91; mol wt, 1307.0; molar conductivity, (acetonitrile), 276.69 ohm^{-1} cm^2.

Bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) Nonachlorodirhenate(III-IV).

Tetra-n-butylammonium nonachlorodirhenate(IV) (0.30 g, 0.321 mmoles) was dissolved in a minimum of methylene chloride and a solution of 1,1-dimethyl-3-oxobutyltriphenylphosphonium hydrogen dichloride (0.60 g, 1.39 mmoles) in 20 ml of ethanol was added. There was no immediate change. In about fifteen minutes the green solution seemed to be turning blue and in about thirty minutes the solution was a deep purple. A small amount of ether was added and the solution was allowed to stand overnight, giving 0.38 g (84.0%) of purple bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) nonachlorodirhenate(III-IV). Consult the Appendix for the infrared and electronic spectra.

Anal. Calcd. for $C_{48}H_{52}P_2Re_2Cl_9$: C, 40.76; H, 3.71; mol wt, 1414.38. Found: C, 40.93; H, 4.01; mol wt, 1345.5.

The Reaction of Rhenium(V) Chloride and Triphenylphosphine in Anhydrous Acetonitrile.

An unweighed amount of rhenium(V) chloride was put into a flask and approximately 40 ml of acetonitrile was added, giving a deep red-orange solution. After swirling the flask for several minutes to ensure dissolution of the rhenium(V) chloride, an unweighed amount of triphenylphosphine was added. The color of the solution changed to a light orange, but no crystals were deposited. After allowing the solution to stand capped, in the dry box for six hours, red crystals were seen to have deposited. The following day the crystals were collected on sintered glass and washed with acetonitrile. The infrared spectrum indicated the crystals to be tetrachlorobis(triphenylphosphine)rhenium(IV).

The Reaction of Rhenium(V) Chloride and Triphenylphosphine in Benzene.

Rhenium(V) chloride (0.3310 g, 0.912 mmoles) was added to 75 ml of benzene. After approximately one hour of intermittent swirling and standing it was observed that some of the rhenium(V) chloride would not go into solution. This rhenium(V) chloride

(0.1930 g, 0.532 mmoles) was filtered by vacuum from the green solution. To the filtrate was added a solution of triphenylphosphine (1.00 g, 1.82 mmoles) in 10 ml of benzene. There was no change in color of the solution, which was then allowed to stand, capped, overnight in the dry box.

After twelve hours, most of the yellow solution was carefully decanted from a purple precipitate, and 9.0 mg (4.3%) of purple bis(triphenylphosphonium) nonachlorodirhenate(III-IV) was collected by centrifugation, washed with benzene, and dried at 20°C and 1 mm Hg. Consult the Appendix for the infrared spectrum of the compound.

Anal. Calcd. for $C_{36}H_{32}P_2Re_2Cl_9$: C, 35.44; H, 2.81. Found: C, 35.27; H, 3.28; molar conductivity, (acetonitrile), 252 ohm^{-1} cm^2.

The yellow solution was concentrated on a rotary evaporator to 15 ml, giving a brown residue. The residue was collected on sintered glass, and washed with diethyl ether, leaving 0.062 g (30.0%) of green trichlorotriphenylphosphinerhenium(III).

Anal. Calcd. for $C_{18}H_{15}PReCl_3$: C, 38.95; H, 2.72. Found: C, 38.90; H, 3.47.

The Reaction of Rhenium(V) Chloride and Triphenylphosphine in Carbon Tetrachloride.

Rhenium(V) chloride (0.1300 g, 0.85 mmoles) was swirled in 75 ml of carbon tetrachloride for one hour. At the end of that time a considerable amount of the material had not dissolved. The green solution was filtered through sintered glass, collecting 0.2312 g (0.622 mmoles) of undissolved rhenium(V) chloride. To the green solution was added a solution of 1.00 g (3.82 mmoles) of triphenylphosphine in 10 ml of carbon tetrachloride. The resulting solution seemed to become somewhat lighter in color, but there was no deposition of crystals.

After allowing the solution to stand overnight, most of the yellow solution was decanted from a small amount of precipitate and then this yellow-green precipitate (3.0 mg) was collected by centrifugation. Concentration of the mother liquor on a flash evaporator failed to give an identifiable product. Consult the Appendix for the infrared spectrum of the compound.

Bis(tetraphenylphosphonium) Hexachlororhenate(IV).

Potassium hexachlororhenate(IV) (0.22 g, 0.46 mmoles) and 15 ml of acetone were refluxed and stirred (magnetic stirrer) in a 50 ml three-necked flask. Once refluxing had started, a suspension of tetraphenylphosphonium chloride (0.40 g, 1.07 mmoles)

in 10 ml of acetone was added. Two ml of water were added and the tetraphenylphosphonium chloride seemed to go into solution. The solution was heated and stirred for two hours and then pale green crystals were collected by filtering through scintered glass. Consult the Appendix for the infrared spectrum of the compound.

Anal. Calcd. for $C_{48}H_{40}P_2ReCl_6$: C, 53.35; H, 4.00. Found: C, 53.18; H, 4.83.

Bis(1,1-dimethyl-oxobutyltriphenylphosphonium) Hexachlororhenate(IV).

Oxotrichlorobis(triphenylphosphine)rhenium(V) (1.20 g, 1.44 mmoles) was suspended in acetone in a three-necked, round-bottomed flask, fitted with a condenser, gas inlet tube, outlet tube, and magnetic stirrer. The suspension was refluxed and hydrogen chloride gas was passed through the solution. After about one hour, the dark reddish-brown solution was cooled and concentrated to one-half of its volume on a water pump. Allowing the concentrated solution to stand overnight gave 0.77 g (48%) green crystals. They were collected on sintered glass, washed with acetone, and recrystallized from methylene chloride-ether, giving 0.69 g (43%) of pale green product. Consult the Appendix for the infrared and nmr spectra of the compound.

Anal. Calcd. for $C_{48}H_{52}P_2O_2ReCl_6$: C, 51.39; H, 4.67; Cl, 18.96; Re, 16.59; mol wt, 1121. Found: C, 51.21; H, 4.43; Cl, 18.86; Re, 16.90; mol wt, 1180; molar conductivity (in acetonitrile), 262 ohm^{-1} cm^2.

The compound was also prepared using potassium hexachlororhenate(IV), (0.60 g, 1.26 mmoles), 15 ml acetone, 5 ml of 12N hydrochloric acid, and triphenylphosphine (0.60 g, 2.30 mmoles) and refluxing the mixture for five hours. Concentrating the solution and filtering through sintered glass gave 0.54 g (38%) of pale green crystals. Recrystallization yielded 0.48 g (34%) of product. Elemental analysis and a comparison of the infrared spectra showed that the product was also bis(1, 1-dimethyl-3-oxobutyltriphenylphosphonium) hexachlororhenate(IV).

A third method to obtain the product was to dissolve 0.10 g of bis(tetraphenylarsonium) hexachlororhenate(IV) in 35 ml of methylene chloride and add a solution of 0.50 g of 1,1-dimethyl-3-oxobutyltriphenylphosphonium hydrogen dichloride in 35 ml of ethanol. The resulting solution was concentrated to 40 ml and 20 ml of hexane was added. The solution was then concentrated on a rotary evaporator until crystallization began. Elemental analysis and the infrared spectrum showed that this was the same compound as obtained in the two foregoing methods.

Attempted Reaction of Tetrachlorobis(triphenylphosphine)-rhenium(IV) and Triphenylphosphine Oxide.

Tetrachlorobis(triphenylphosphine)rhenium(IV) (0.2028 g, 0.237 mmoles) was combined with triphenylphosphine oxide (0.4366 g, 1.57 mmoles) in a three-necked 50 ml flask. The flask and its contents were flushed well with dry nitrogen. Acetone, dried as usual over molecular sieves, was distilled into the flask. The flask was then stoppered, and set up to reflux under nitrogen, with stirring provided by a magnetic stirrer. After refluxing and stirring for two days, the undissolved crystals were collected on sintered glass. After washing, the infrared spectrum showed the red crystals to be the starting material, tetrachlorobis(triphenylphosphine)rhenium-(IV).

1,1-Dimethyl-3-oxobutyltriphenylphosphonium Hydrogen Dichloride.

Anhydrous diethyl ether (20 ml) was carefully distilled into a dried, three-necked, round-bottomed 100 ml flask, and to this was added 5 ml of mesityl oxide. The flask was fitted with a gas inlet tube and a gas outlet tube which had a calcium chloride tube. The flask and its contents were thoroughly chilled in an ice-salt bath ($-5^{o}C$) and stirred by means of a magnetic stirrer. Hydrogen chloride gas was bubbled through the mixture for one and one-half hours. At the end of that time the hydrogen chloride was turned off and a solution

of triphenylphosphine (13 g, 49.6 mmoles) in 60 ml of diethyl ether was added, dropwise. There was an immediate precipitation of a white, gummy material. This was collected by suction filtration and washed with diethyl ether to give 9.0 g (46%) of product. A number of attempts were made to recrystallize the material from various solvents without success. The material was purified by refluxing in diethyl ether for two days, giving 7.9 g (40%) of white crystalline product. Consult Appendix for the infrared and nmr spectra of the compounds.

Anal. Calcd. for $C_{24}H_{27}POCl_2$: C, 66.52; H, 6.05; Cl, 16.36; mol wt, 433. Found: C, 66.76; H, 6.43; Cl, 16.43; mol wt, 357; molar conductivity (acetonitrile), 90 ohm^{-1} cm^2.

3-Pentene-2-one.

The preparation followed the outline of Patrick (55). To 100 ml of saturated sodium chloride solution there was added sodium hydroxide (12 g, 0.30 moles). When the base had dissolved with stirring, the precipitated sodium chloride was removed by filtration. This filtrate, 200 ml of diethyl ether, and acetone (194 g, 3.35 moles) were placed in a one liter, three-necked flask fitted with stirrer and thermometer. The stirred mixture was cooled with an ice bath and a solution of acetaldehyde (152 g, 3.45 moles) in acetone

(194 g, 3.35 moles) was added dropwise, such that the temperature was maintained between 10 and 12°C. IMPORTANT: The solution should be well stirred for complete reaction to take place. The mixture was stirred for 15 minutes after the acetaldehyde-acetone solution had been added and then the ice bath was removed and the mixture stirred 15 minutes more. The aqueous (lower) layer was removed and the organic layer carefully neutralized with 85% phosphoric acid. The color changed to yellow. The solution was dried over calcium chloride which caused the solution to darken. The solution was filtered from the calcium chloride and stored in a refrigerator overnight.

The next day the low boiling component was removed by distillation up to 60°C at slightly reduced pressure. Then 1 ml of sulfuric acid (36 N) was added and distillation was continued, collecting water and product up to 120°C and lower pressure, although the pressure was too great to be read on the manometer in use. (Patrick (55) states "up to 105°C/200mm"). Anhydrous potassium carbonate was added to the distillate until saturated and the organic layer was separated, dried over potassium carbonate, and fractionated. The distillate, bp. 56-124°C, 1 atm, was refluxed with 40 ml of hexane in a Dean-Stark trap to remove water and then distilled. The yellow fraction, bp. 115-124°C, was collected. It was redistlled to give 46 g (15.65%) of

faintly yellow product. bp. 117-120°C; n_D^{25}, 1.4336.

Patrick (55): bp. 119-121°C; n_D^{25}, 1.4341.

1-Methyl-3-oxobutyltriphenylphosphonium Hydrogen Dichloride.

Anhydrous diethyl ether (30 ml) was carefully distilled into a dried, three-necked, round-bottomed 100 ml flask, and to this was added 3-pentene-2-one (1.9 g, 22.6 mmoles). The flask was fitted as described in the mesityl oxide reaction. The flask and its contents were thoroughly chilled in an ice salt bath (-5°C) and stirred by means of a magnetic stirrer. Hydrogen chloride gas was bubbled through the mixture for one hour. At the end of that time the hydrogen chloride was turned off and a solution of triphenylphosphine (6 g, 22.8 mmoles) in 50 ml of ether was added, dropwise. A white precipitate appeared and, after the addition of the triphenylphosphine solution had been completed, 2.5 g (26.4%) of gummy white product. The original filtrate was allowed to air-evaporate to three-fourths the original volume and 4.85 g (51.2%) more of the product was collected and washed with diethyl ether. Refluxing of the product under diethyl ether for two days gave 4.56 g (48.0%) of white, crystalline product. Consult the Appendix for the infrared and nmr spectra.

Anal. Calcd. for $C_{23}H_{25}POCl_2$: C, 65.88; H, 6.01; Found: C, 65.78: H, 5.60.

1,1-Dimethyl-3-oxobutyltriphenylphosphonium Bromide.

Anhydrous diethyl ether (20 ml) was distilled into a dried, three-necked, round-bottomed 100 ml flask, and to this was added 2.5 ml of mesityl oxide. The flask was fitted with a gas inlet tube and a gas outlet tube which had a calcium chloride tube. The flask and its contents were thoroughly chilled in an ice-salt bath ($-5^{o}C$) and stirred by means of a magnetic stirrer. Hydrogen bromide gas was bubbled through the mixture for one hour. At the end of that time the hydrogen bromide was turned off and a solution of triphenylphosphine (6.5 g, 24.8 mmoles) in 40 ml of diethyl ether was added, dropwise. There was an immediate precipitation of a pale orange, gummy material. This was collected by suction filtration and washed with diethyl ether to give 5.2 g (40.3%) of product. The material was purified by refluxing in diethyl ether for two days, to give 4.1 g (31.6%) of pale orange crystalline product.

Anal. Calcd. for $C_{24}H_{26}POBr$: C, 65.31; H, 5.94; Found: C, 64.72; H, 5.95.

Retention of Triphenylphosphine and Triphenylphosphine Oxide on an Alumina Column.

Triphenylphosphine or triphenylphosphine oxide was dissolved in 10 ml of benzene or acetone and eluted down a 17 cm column of

alumina with 150 ml of the same solvent. The eluted material was collected, 50 ml at a time, evaporated to dryness on a flash evaporator, and weighed to determine when, if at all, the triphenylphosphine and triphenylphosphine oxide were passing through the column. A fresh column of alumina was used for each run.

Results Using Acetone:

	Triphenylphosphine	Triphenylphosphine oxide
Starting weight	1.2571 g	1.1944 g
First 50 ml	1.2233 g	1.0278 g
Second 50 ml	0.0149 g	0.0806 g
Third 50 ml	0.0094 g	0.040 g
Total	1.2476 g	1.1490 g

Results Using Benzene:

Starting weight	0.5959 g
First 50 ml	0.1504 g
Second 50 ml	0.0400 g
Third 50 ml	0.0119 g
Total	0.2193 g

RESULTS AND DISCUSSION

Rhenium(V) Chloride and Triphenylphosphine in Acetone.

This system was chosen for the initial study for two reasons. First, rhenium(V) chloride is soluble in acetone and conceivably could abstract oxygen from it. Second, many rhenium complexes of triphenylphosphine had been correctly identified and would facilitate product identification.

The reaction yielded two products which were readily characterized. The first was oxotrichlorobis(triphenylphosphine)rhenium(V), obtained in variable quantities depending upon reaction conditions. This compound was readily identified by a strong band in its infrared spectrum at 969 cm^{-1}, characteristic of the rhenium-oxygen stretching mode (56).

The two possible sources for the oxygen in the complex are water and acetone. Experimental evidence suggesting water as the source of the oxygen is the observation that addition of water to the acetone results in an increased yield of oxotrichlorobis(triphenylphosphine)-rhenium(V). In the course of this study, Grove and Wilkinson (34) also examined the reaction and obtained the same product. They observed that the dissolution of rhenium(V) chloride in acetone gave a green solution and attributed the green color to the formation of oxotrichloro-rhenium(V), obtained from the reaction of rhenium(V) chloride and water.

This product was obtained even when great care was taken to exclude moisture. This observation would seem to indicate that oxygen was being abstracted from the acetone. However, Allen et al. (57) have recently studied the reaction of rhenium(V) chloride with such oxygenated solvents as tetrahydrofuran, dioxane, and thioxane and found that, rather than abstract oxygen, the rhenium formed simple coordination compounds with these solvents. While this does not exclude the possibility of oxygen abstraction from acetone, it indicates that water is the more likely source of oxygen.

The other readily identified product from the reaction was tetrachlorobis(triphenylphosphine)rhenium(IV). This compound was easily distinguished by its red color, ease of elution from a chromatography column and the infrared spectrum. It was observed that shortly after the formation of oxotrichlorobis(triphenylphosphine)rhenium(V), either a red coloration was formed on the surface of the green solid or the green product was being converted to tetrachlorobis(triphenylphosphine)rhenium(IV). Rouschias and Wilkinson (58) have reported such a conversion as given by the following reaction:

$$3ReOCl_3(PPh_3)_2 \longrightarrow 2ReCl_4(PPh_3)_2 + ReO_3Cl + 2PPh_3.$$

However, there was an important difference between the two systems. The latter was heated, while the former was maintained at room temperature. The infrared spectrum of the product had a strong band at 969

cm^{-1}, indicating that the oxotrichlorobis(triphenylphosphine)rhenium-(V) was precipitated first and covered by subsequent precipitation of tetrachlorobis(triphenylphosphine)rhenium(IV). It has been observed that the latter compound is slightly soluble in room temperature acetone, whereas the former is almost totally insoluble. Thus, that the oxotrichlorobis(triphenylphosphine)rhenium(V) precipitated first was not unexpected.

The filtrate from the original reaction mixture, upon chromatographic separation, yielded a yellow compound and a purple component which were very difficult to formulate. The yellow compound had the rather unusual property (for an inorganic complex) of being quite fluffy. The infrared spectrum had several regions of particular interest. There was a strong peak at 1718 cm^{-1}, the area usually associated with a doubly bonded carbon to oxygen stretching frequency. For example, the carbon-oxygen stretching frequency of free acetone is 1712 cm^{-1} (59). Two possibilities were considered to account for the band. One was the coordination of acetone to rhenium. However, such coordination should weaken the carbon-oxygen bond and thus lower the frequency of the absorption (59). Since it was not lowered this would indicate that the acetone was very weakly bound, or perhaps just trapped in the

crystal. In such a case, recrystallization or pumping in vacuum should remove the acetone. Neither method resulted in the diminution of the band at 1718 cm^{-1}. The existence of a bridging carbonyl was ruled out, as no known complex of this type exhibited a band at this low a frequency.

Another band of interest occurred at 1100 cm^{-1} with a shoulder at 1087 cm^{-1}. This band was in the region for the x-sensitive mode of coordinated triphenylphosphine (60) but higher than those seen in the two coordination compounds or rhenium previously considered. In both of these the band occurs at approximately 1090 cm^{-1}.

Finally, there was a band at 720 cm^{-1} observed as a very strong band in all triphenylphosphine oxide complexes and assigned to an x-sensitive mode (60). However, its intensity in the yellow complex was weak compared to that found in triphenylphosphine complexes. Other workers, noting its presence in phosphonium salts, claimed it to be characteristic of four-coordinate phosphorus (61).

It was observed that when a high yield of the yellow compound was obtained the yield of oxotrichlorobis(triphenylphosphine)rhenium-(V) was small. This suggested that the former was produced from the latter. In addition, the reaction of rhenium(V) chloride with water yielded hydrogen chloride as one of the products, so it was decided to attempt to react the oxotrichlorobis(triphenylphosphine)rhenium(V) with

hydrogen chloride in acetone, in an attempt to synthesize the yellow compound. This reaction yielded a pale green compound whose infrared spectrum was very similar to that of the yellow compound, except that the shoulder at 1089 cm^{-1} was absent. Further, the carbon-hydrogen analyses were virtually the same.

At first it was felt that the yellow and pale green compounds were the same. Also, it was found that the pale green compound could be prepared from triphenylphosphine, potassium hexachlororhenate(IV), and hydrogen chloride in boiling acetone. Conductivity measurements indicated the yellow and green compounds to be salts. Further, the nmr of the green compound showed two different types of methyl protons as well as methylene and phenyl protons.

In an effort to gain further information regarding the cation of these salts, the mother liquor from the oxotrichlorobis(triphenylphosphine)rhenium(V)-hydrogen chloride reaction was vacuum distilled, yielding a liquid which was soon identified as phorone, $(CH_3)_2C = CH-C(O)-CH=C(CH_3)_2$.

Phorone is the result of the condensation of three molecules of acetone. Such a condensation occurs in the acidic media, by means of the well-known Aldol condensation (62). Although phorone itself was of no value with regards to the formulation of the compounds in question, its presence led to the correct formulation. The mode of

formation was given as follows:

a) $2CH_3C(O)CH_3 \xrightarrow{HCl} CH_3C(O)CHC(CH_3)_2$

b) $CH_3C(O)CHC(CH_3)_2 \xrightarrow[H^+]{} CH_3\overset{OH^+}{\overset{\|}{C}}CH{=}C(CH_3)_2$

c) $CH_3\text{-}C(OH^+){=}CHC(CH_3)_2 \xrightarrow{PPh_3} CH_3\text{-}C(OH^+){=}CHC(CH_3)_2PPh_3$

d) $CH_3\text{-}C(OH^+){=}CHC(CH_3)_2PPh_3 \longrightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}{=}CH_2\text{-}C(CH_3)_2PPh_3$

It was postulated that the rhenium(V) chloride was catalyzing the condensation of two moles of acetone to form mesityl oxide and water. The water, in turn, could attack the rhenium(V) chloride to form hydrogen chloride. This mechanism could account for the formation of the phosphonium salt and the $ReOCl_3(PPh_3)_2$ in systems which were thought to be anhydrous.

This cation formulation explained the infrared spectra of the compounds. The bands at 720 cm^{-1} and 1100 cm^{-1} were readily attributed to a phosphonium salt (61), (63) and the absorption at 1718 cm^{-1} was due to a simple carbonyl moeity.

From the structure of the cation the nmr could be readily explained. The doublet centered at 1.8 delta was attributable to the two methyl groups which were beta to the phosphorous and due to H-^{31}P coupling. The coupling constant and chemical shift were in good agreement with

those found by Seyferth, Eisert, and Heeren (64), delta = 1.68 and J = 17.2, for $(CH_3)_3CP(C_6H_5)_3$ Br. The singlet at 2.1 delta arose from the methyl group adjacent to the carbonyl group. The methylene group at 2.8 delta appeared as a doublet due to H-^{31}P coupling. The coupling constant was smaller in this beta position due to the deshielding effect of the carbonyl group which was alpha to the methylene group. This signal was also complicated by the possible magnetic nonequivalence of the protons adjacent to an asymmetric center (65). The multiplet at 7.7 delta was assigned to the phenyl group and was in the same position found by Kaesz, et al. (66). There was a broadening of all signals due to the presence of the paramagnetic rhenium ion. A comparison of the nmr date for bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) hexachlororhenate(IV) and the corresponding hydrogen dichloride salt showed only one significant shift. This isotropic shift for the methylene group is not clearly understood at the present time because of a lack of knowledge of the stereochemistry of the cation, but a molecular model suggests the shift may be due to shielding of the methylene group by the phenyl rings.

There remained to take the experimentally determined molecular weight with the elemental analyses and subtract that part contributed by the cation to formulate the anion as pentachlorotriphenylphosphinerhenate(IV), $(ReCl_5PPh_3)^{1-}$.

This formulation cleared the one remaining problem with the infrared spectrum which was the doublet at 1100 cm^{-1} and 1087 cm^{-1}. The band at 1100 cm^{-1} was assigned to the x-sensitive mode of the phosphonium salt, as mentioned, and the band at 1087 cm^{-1} was the x-sensitive mode of the coordinated triphenylphosphine in the anion. This anion had been previously isolated as the triphenylphosphonium salt (67).

To provide an alternate method of synthesis of the yellow compound, an independent preparation of the hydrogen dichloride salt of the phosphonium cation and the triphenylphosphonium salt of the pentachlorotriphenylphosphinerhenate(IV) salt followed. These two, when dissolved in appropriate solvents and combined, gave a compound identical in all regards to the yellow compound from the rhenium(V) chloride reaction. Thus, the compound was formulated as 1,1-dimethyl-3-oxobutyltriphenylphosphonium pentachlorotriphenylphosphinerhenate(IV).

Further consideration of the evidence at hand, and particularly the fact that the green compound could be obtained from the reaction of hydrogen chloride, triphenylphosphine, potassium hexachlororhenate, and acetone led to the conclusion the green compound was bis-(1,1-dimethyl-3-oxobutyltriphenylphosphonium) hexachlororhenate(IV).

This explained its color, as pale green is the color found in many hexachlororhenate(IV) salts. Also, it explained why there was no absorption in the infrared at 1089 cm^{-1} as there was in the yellow compound.

The question of the identity of the purple component was considered next. The similarity of the infrared spectrum of the purple component and the yellow compound indicated that the same cation was present. Conductivity measurements offered support to the belief that the compound was a salt.

Much of the difficulty in characterizing this compound was due to erratic carbon-hydrogen analyses. The early analyses ran from 42 to 45 percent carbon and 3.5 to 4.3 percent hydrogen. The problem was attributed to the method of separating the purple component from possible impurities. When the acetone mother liquor was passed down the column, it was noted that the purple band stopped when the elution of the yellow compound was complete. Further washing with acetone failed to elute additional purple material. It was found that the recalcitrant purple compound could be removed using acetonitrile and this method provided a solid which gave consistent carbon and hydrogen analyses.

While this work was underway, Bonati and Cotton (44) reported the existence of the dinuclear species, blue octachlorodirhenate(III),

purple nonachlorodirhenate(III-IV), and green nonachlorodirhenate-(IV). To explain the observed elemental analyses, infrared spectrum, electronic spectrum, and conductivity we were led to the consideration that one of these was the anion present in the purple component. The octachlorodirhenate(III) has one strong absorption in its visible absorption spectrum at 685 mμ while the nonachlorodirhenate(III-IV) has two absorptions, one at 736 mμ and one at 537 mμ.

The purple component had a visible spectrum similar to the nonachlorodirhenate(III-IV) ion, with absorptions at 720 mμ and 539 mμ. After allowing the solution of the purple component to stand for two days, the peak at 720 mμ was observed to be covered by a band centered at 682 mμ and of greater intensity, while the band at 539 mμ decreased in size. This indicated the conversion of nonachlorodirhenate(III-IV) ion to octachlorodirhenate(III) ion. Such a conversion has been observed in acetone and acetonitrile (36).

The identification of the purple mixture was corroborated by preparing both bis(tetra-n-butylammonium) octachlorodirhenate(III) and bis(tetra-n-butylammonium) nonachlorodirhenate(III-IV) and reacting these with 1,1-dimethyl-3-oxobutyltriphenylphosphonium hydrogen dichloride to obtain bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) octachlorodirhenate(III) and the corresponding

nonachlorodirhenate(III-IV). Further, by following the flow sheet of Bonati and Cotton (44), it was shown that these species were interconvertable. The only deviation from the flow sheet was that the green intermediate, nonachlorodirhenate(IV), could not be isolated as the 1,1-dimethyl-3-oxobutyltriphenylphosphonium salt.

In an effort to better establish the spectral evidence, a mixture of pure bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) nonachlorodirhenate(III-IV) and the corresponding salt of octachlorodirhenate(III) were mixed together and the spectrum of the solution observed. It was essentially that of the purple which had stood in solution for two days. The ultraviolet spectra were also observed but the absorption of the phenyl groups dominated this area. Thus, the purple component was finally formulated as a mixture of bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) octachlorodirhenate(III) and the corresponding nonachlorodirhenate(III-IV) salt. It seems reasonable that the nonachlorodirhenate(III-IV) is fairly soluble in acetone and remains in solution long enough to undergo partial conversion.

There are two contaminants in the purple component besides 1,1-dimethyl-3-oxobutyltriphenylphosphonium pentachlorotriphenylphosphinerhenium(IV) which should be considered. The first and most obvious is triphenylphosphine or triphenylphosphine oxide. As the

Experimental Section shows, however, these compounds are only very weakly held to the column and should have largely passed through before even the first part of the purple compound was collected. They would be much more likely to appear as a contaminant in the yellow compound.

The other possibility is bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) hexachlororhenate(IV). However, this material is poorly soluble in acetone and, if formed at all in such systems, should have precipitated along with oxotrichlorobis(triphenylphosphine)-rhenium(V). However, there has never been any evidence for the formation of this compound in the system under discussion.

Unfortunately, direct evidence for the presence of 1,1-dimethyl-3-oxobutyltriphenylphosphonium pentachlorotriphenylphosphinerhenate-(IV) as the impurity is lacking. A small band in the infrared spectrum of one of the purple samples whose analysis was high indicated the presence of the yellow compound. Results from the electronic spectra are inconclusive as absorptions of the purple component masks all absorptions due to 1,1-dimethyl-3-oxobutyltriphenylphosphonium pentachlorotriphenylphosphinerhenate(IV).

Further evidence for the presence of nonachlorodirhenate(III-IV) ion in an acetone solution of rhenium(V) chloride was provided by Allen, *et al.* (38).

The work described herein does not agree with the report of Grove and Wilkinson (37) in a similar system, which appeared while this work was underway. To ascertain what relationship, if any, Grove and Wilkinson's products had to those reported in this work, their work was carefully repeated. The Experimental Section contains a full account of this reaction. Our reaction followed that of Grove's in all regards save the color of "isomer 2", which was purple in our hands, green in theirs.

The important point is that, as the work in the Experimental Section shows, both Grove's "isomers" were in fact readily resolvable into two compounds, which fit those previously formulated as yellow 1,1-dimethyl-3-oxobutyltriphenylphosphonium pentachloro-triphenylphosphinerhenate(IV) and the purple mixture of bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) nonachlorodirhenate(III-IV) and bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) octachloro-dirhenate(III). The greatly increased total volume of "isomer 2" reported by Grove is readily accountable in terms of the vacuum and heat applied on the "isomerization" process merely tearing the more flocculent yellow compound loose from the purple compound. Further, the color of the "isomer 2", green, could be a blending of the proper proportion of yellow and purple. They report the carbon-oxygen stretch frequency at 1712 cm^{-1}, essentially the same place for the two

compounds reported herein. Finally, there has been no instance of a compound fitting the description of that reported by Grove and Wilkinson which has not been resolvable into the yellow and purple compounds above.

The only other study of the rhenium(V) chloride-triphenylphosphine system in acetone was by Johnson, et al. (33) who reported the formation of tetrachloro(triphenylphosphine)rhenium(IV), $[ReCl_4(PPh_3)]_n$. It was found to be insoluble in all common solvents and was thought to be a polymer. Our studies were unable to confirm the existence of this product.

Hydrogen Dichloride Ion.

The reaction of triphenylphosphine, mesityl oxide, and hydrogen chloride in dry ether gave a compound which had a carbon-hydrogen analysis too low to fit the expected 1,1-dimethyl-3-oxobutyltriphenylphosphonium chloride, while the chloride analysis was greater than calculated. The infrared spectrum seemed rather unusual with a series of rather ill-defined absorptions in the region of 1100 - 600 cm^{-1}, and nmr of the compound indicated the presence of a proton with a value of 12.3 delta, which means that the proton was quite deshielded. Consideration of all these factors led to the formulation of the compound as 1,1-dimethyl-3-oxobutyltriphenylphosphonium hydrogen dichloride.

The nmr spectrum was analyzed as follows: The signal found at 12.3 delta in trideuteroacetonitrile is attributed to the proton of hydrogen dichloride ion. It showed a marked concentration dependence, shifting to 8.7 delta upon dilution. This kind of concentration dependence has been noted previously for the hydrogen dichloride ion (68). If the solution is allowed to stand in the nmr tube the peak will broaden and gradually disappear. This, as well as the concentration dependence, has been attributed to a rapid exchange of hydrogen: $HCl_2^- + S \rightleftharpoons HS^+ + 2Cl^-$, where S is the solvent. This equilibrium gives a chemical shift which is the average of that for the two species involved (69). In deuterochloroform, a value of 12.4 delta was obtained which is changed by only 0.1 delta upon dilution and does not broaden or disappear upon standing.

The infrared spectrum of the hydrogen dichloride ion was the basis for a paper by Evans and Lo (70) in which the hydrogen dichloride ions were described as either Type I or Type II salts. The Type I structure is an asymmetric, linear structure, of C_{2v} symmetry. The Type II salts were regarded as linear, symmetric structures, of $D_{\infty h}$ symmetry. Nibler and Pimentel (71) re-examined these claims and decided that, while the Type I structures were certainly not C_{2v} or $D_{\infty h}$ (centrosymmetric), the

Type II salts were better interpreted as possessing C_{2v} symmetry. The 1,1-dimethyl-3-oxobutyltriphenylphosphonium hydrogen dichloride spectrum seemed to be comparable in the region 1200 cm^{-1} to 600 cm^{-1} to the Type II salts.

Rhenium(V) Chloride and Triphenylphosphine in Acetonitrile.

During this study this reaction was reported by Roushias and Wilkinson (58). The product isolated was tetrachlorobis-(triphenylphosphine)rhenium(IV) and we are in agreement with this formulation.

Rhenium(V) Chloride and Triphenylphosphine in Carbon Tetrachloride.

This reaction gave a minute amount of a compound which was not characterized. From the complexity of the infrared spectrum, it would appear that the solvent was again incorporated in the product in some way.

Rhenium(V) Chloride and Triphenylphosphine in Benzene.

Rhenium(V) chloride exhibited only limited solubility in benzene, giving a green solution. Addition of triphenylphosphine to this solution gave a small amount of a purple compound whose infrared spectrum indicated a triphenylphosphonium salt. The compound showed the P-H peak at 2380 cm^{-1}, attributable to a phosphorus-hydrogen stretching mode, a shoulder at 900 cm^{-1} and a peak at 880 cm^{-1} associated with phosphorus-hydrogen bending (61).

In addition, there was a band at 720 cm^{-1}, associated with phosphonium salts.

The conductivity in acetonitrile showed the compound to be a salt and the electronic spectrum indicated that the anion was nonachlorodirhenate(III-IV). Thus, the compound could be formulated as bis(triphenylphosphonium) nonachlorodirhenate-(III-IV), $(Ph_3PH)_2Re_2Cl_9$.

While concentrating the mother liquor, a green insoluble species was obtained whose infrared spectrum and elemental analysis fit well for trichloro(triphenylphosphine)rhenium(III). The infrared spectrum of this compound showed no absorptions in the region of 975 cm^{-1} indicating the absence of the usual rhenium to oxygen bond. Because of the highly insoluble nature of the material, it must have been formed after the purple compound was filtered from solution.

Cotton, Curtis, and Robinson (72) obtained trichloro(triphenyl-phosphine)rhenium(III) in 98 percent yield by reacting the octachloro-dirhenate(III) ion with triphenylphosphine. Since it was produced from the dimeric octachlorodirhenate(III) ion, the most probable formulation was the dimer, $(ReCl_3PPh_3)_2$. The insolubility of the compound prevented further investigation. Cotton and Foxman (73) were able to prepare the more tractable hexachlorobis(triethylphosphine)dirhenium(III)

and, from x-ray analysis, showed it to be a substitution product of octachlorodirhenate(III). See Figure 5.

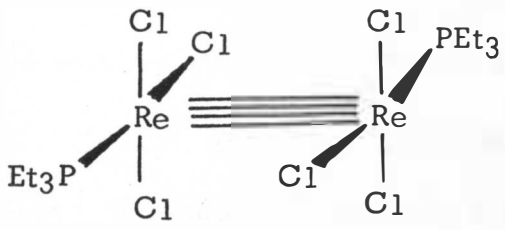


Figure 5.

Rhenium(V) Chloride and Pyridine in Acetone.

As discussed in the Historical Section, this reaction has been investigated several times, although never under anhydrous conditions. Under these conditions, there was no trace of the green μ-oxodioxotetrachlorotetrakis(pyridine)dirhenium(V). The only product isolated was the orange dioxotetrakis(pyridine)rhenium(V) chloride dihydrate.

There are three possibilities for the source of the oxygen incorporated into the product. First, as has been shown, rhenium(V) chloride causes acetone to condense, giving mesityl oxide and water. The water could then react with the rhenium(V) chloride to give the oxo-species. Secondly, there is the possibility that the system was not completely anhydrous. Thirdly, the rhenium(V) chloride may have

been slightly hydrolyzed before the reaction was run. Further work on the system is necessary to determine the source of the oxygen. Also, investigation is warranted to explain why pyridine causes the loss of all the chlorine atoms from the coordination sphere of the rhenium, which was not observed with any other ligand.

Rhenium(V) Chloride and Triphenylphosphine Oxide in Acetone.

The reaction of rhenium(V) chloride and triphenylphosphine oxide also yielded only one isolatable product. Conductivity measurements indicated the compound to be a salt and identification of the anion as nonachlorodirhenate(III-IV) was obtained in the manner previously described for the bis(triphenylphosphonium) nonachlorodirhenate(III-IV).

The cation was more difficult to characterize. The infrared spectrum showed a strong band at 1115 cm^{-1}, bands at 750 cm^{-1} and 690 cm^{-1} associated with the carbon-hydrogen out-of-plane deformation and the out-of-plane ring deformation, respectively (60). In addition, there was a very strong band at 720 cm^{-1}, which is always seen in triphenylphosphine oxide adducts (60). A broad peak centered at 900 cm^{-1} was the most puzzling feature of the spectrum. Such broad peaks are often associated with decomposition but this was ruled out when the peak remained after recrystallization. This absorption was similar to that

observed for the hydrogen dichloride ion and was therefore attributed to a symmetrically bonded proton. Unfortunately, the compound was not sufficiently soluble to locate the proton by nmr.

Speakman and Mills (74) have offered two types of formulations for such a system. Type A is a symmetric species where the two molecules are related by a symmetry element, across which they are linked by a hydrogen bond involving the acidic hydrogen atom. In the Type B structures the two linked species are crystallographically distinct, with an unsymmetric hydrogen bond. Neutron diffraction of potassium hydrogen bisphenylacetate (75) and potassium hydrogen maleate (76), both of which had features of the Type A salts, gave results best interpreted as structures containing symmetrically bonded protons.

The infrared spectrum of the Type A structures are characterized by a broad, strong absorption centered at about 900 cm^{-1} and the almost complete absence of absorption around 3300 cm^{-1}, the region for the hydrogen to oxygen stretch frequency. The infrared spectrum of the triphenylphosphine oxide complex was quite consistent with the type of spectrum associated with Speakman's Type A salts.

The cation bis[μ-hydrogen-bis(triphenylphosphine oxide)] was first reported by Hadzi (77). The bromide salt of this ion, prepared by the method outlined in the literature, gave a compound whose

infrared spectrum, 4000 cm^{-1} to 650 cm^{-1}, was superimposable on that of the rhenium compound. It is of interest to remark that the triphenylphosphine oxide compounds prepared by Hadzi (77) all showed spectra characteristic of the Type B, or asymmetric hydrogen bonding, while those prepared in this laboratory by the directions of Hadzi were of the Type A. It was found, however, that the compound of the Type A could be converted to one of Type B by boiling in ether. Efforts to make the chloride salt failed.

A question regarding the influence of the Evans and Lo (70) vs. Nibler and Pimentel (71) disagreement about the linearity of the hydrogen dichloride system on this hydrogen bonded system should be considered. Speakman (74) pointed out that, in the case of several of the systems under his consideration, the proton may not form a straight line with the two electronegative atoms. The important point is that the Type A structure, the characteristics of which the triphenylphosphine oxide compound shows, be symmetric, or to repeat Speakman's criterion, have the two oxygen atoms related by a symmetry element, across which they are linked by a hydrogen bond involving the acid hydrogen atom. In the case of $D_{\infty h}$ symmetry, the symmetry element is the center of invasion and in the case of C_{2v} symmetry, the symmetry element is a plane, perpendicular to the axis joining the two oxygen atoms. Thus, the

interpretation of the infrared spectrum of the triphenylphosphine oxide compound depends upon the symmetry about the hydrogen atom and not the linearity of the system. Either Evans and Lo's linear system or Nibler and Pimentel's bent formulation possesses the necessary symmetry element.

Infrared Spectra of Hexachlororhenate(IV) Salts.

During the investigation of bis(1,1-dimethyl-3-oxobutyl-triphenylphosphonium) hexachlororhenate(IV), the region from 350 cm^{-1} to 250 cm^{-1}, containing the rhenium-chlorine asymmetric stretching frequency, was examined. A lack of information on this frequency and discrepancies regarding the position of this mode reported in the literature necessitated a careful examination of this region for a number of salts of hexachlororhenate(IV).

In general, the compounds showed only one strong peak, which was of an asymmetric nature, featuring a shoulder on the high frequency side which was almost as intense as the main peak. The symmetry of the peak could be due to several factors, such as the site symmetry differing from the point symmetry of the molecule, causing a relaxing of the selection rules, or a deviation from octahedral symmetry. Either case would cause a removal of degeneracy and concomitant activation of otherwise forbidden modes (77), (78).

The peaks of all these compounds were observed to have a shoulder of medium intensity on the low frequency side of the main peak. The possibility that the low frequency shoulder was due to the presence of ^{37}Cl was raised, but the shoulder appeared 10-20 cm^{-1} below the main peak while the observed range for Re-^{37}Cl splitting was 5-8 cm^{-1} (79), (80), (81), (82).

In one case, that of bis(tetraphenylarsonium) hexachlororhenate(IV), a definite splitting was observed, while the splitting previously reported for the potassium (83) and tetraethyl (50) salts was not observed. To determine if the splitting was due to solid-state interaction, bis(tetraphenylarsonium) hexachlororhenate(IV) was examined in acetonitrile. Only one peak, with no fine structure, was observed and thus it seems that the splitting seen in the solid state could be attributed to solid-state interaction.

The disagreement with the values cited in the literature can be attributed to several factors. The method of preparation is the first such possibility. The spectrum of bis(tetraethylammonium) hexachlororhenate(IV) did not show the splitting observed by Chatt, et al. (50) though the experimental procedure outlined by Chatt was followed. It is possible that slightly different crystal structure could have occurred upon crystallization. This sort of occurrence has been reported by Cotton and Johnson (83) who found that

ammonium hexachlororhenate(IV) grew as large green octahedra, red-brown octahedra, and small yellow crystals, all from the same reaction vessel. They attributed this to growth occurring at different times and therefore under different physical and chemical conditions during the preparation.

Particularly troublesome was the discovery that variations in the operating conditions of the instrument, conditions not usually reported in the literature, could cause variations in the position of the peak under consideration. For example, a change in the speed of the scan would cause a shift of 4-5 cm^{-1} in a given peak in the low frequency area being studied.

Thirdly is the author's own interpretation of where the peak maximum actually lies, in the case of an asymmetric band. Finally, there are the variations in sample preparation to be considered. This was shown when one mull of bis(diethylammonium) hexachlororhenate(IV) showed maxima at 313 cm^{-1} and 293 cm^{-1} while a second mull of the same sample had a peak at 293 cm^{-1}.

The study also demonstrated the variation in the position of the peak with the size of the cation. As the size of the cation was increased, the position of maximum absorption shifted to lower frequency. See Table V. This is in agreement with that previously observed by Adams and Morris (81). This

Table V. Infrared spectra of Hexachlororhenate(IV) salts[a,b].

Cation	Frequency
$[C_5H_6N]^+$	334(w, sh), 303 vs, 287 vs, 275(m, sh)
$[(C_6H_5)_4As]^+$	306 s, 289 vs, 280(m, sh) 303 vs[c]
$[(C_6H_5)_4P]^+$	337(w, sh), 300(s, sh), 289 vs, 275(m, sh)
$[(C_2H_5)_2(C_6H_5)PH]^+$	340(w, sh), 302(s, sh), 291 vs, 278(m, sh)
$[(C_6H_5)_3PH]^+$	338 w, 303(s, sh), 293 vs, 275(m, sh)
$[(C_2H_5)_2NH_2]^+$	301(s, sh), 293 vs, 275(m, sh)
$[CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{CH_3}{\overset{\|}{\underset{CH_3}{\underset{\|}{C}}}}-P(C_6H_5)_3]^+$	302(s, sh), 294 vs, 275(m, sh)
$[CH_3(C_6H_5)_3P]^+$	340 w, 301(s, sh), 294 vs, 275 (m, sh)
$[(C_2H_5)_4N]^+$	301(s, sh), 294 vs, 275(m, sh)
$[(C_2H_5)_4N]^+$ [d]	314, 300
$[p\text{-}CH_3C_6H_4NH_3]^+$	316(s, sh), 303 vs, 275(m, sh)
Cs^+ [e]	313 vs
Rb^+ [f]	319
K^+	326(s, sh), 316 vs, 282(m, sh), 256 w
K^+ [g]	331.6 vs, 319 vs
K^+ [h]	321

a) Nujol mull or KBr pellet, 1X scale; b) vs = very strong, s = strong, w = weak, sh = shoulder; c) acetonitrile solution; d) ref. 50; e) ref. 87; f) ref. 88; g) ref. 84; h) ref. 89.

interpretation is valid only for an isomorphous series. The lowest occuring peak in the series presented is that of the bis(pyridinium) hexachlororhenate(IV), but this compound does not have the potassium hexachloroplatinate structure (84), found for many of the salts under consideration here.

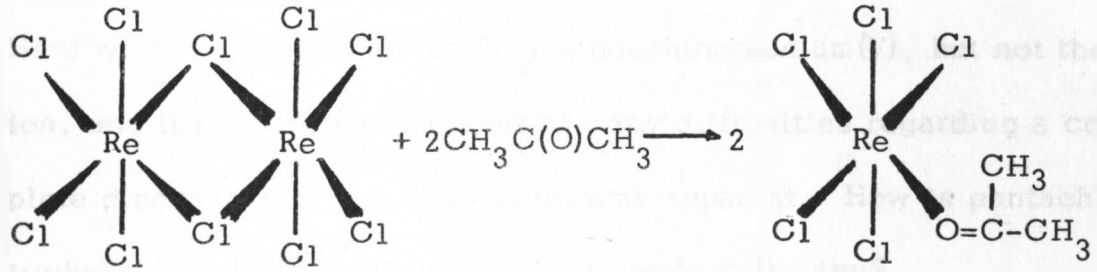
Rhenium(V) Chloride.

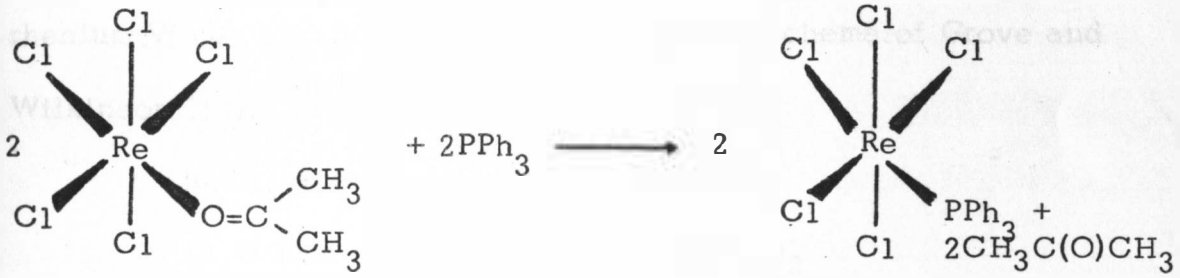
This section was originally intended to provide possible reaction mechanisms which would account for the products isolated from the various reactions previously discussed and the behavior of rhenium(V) chloride in solution. As attempts to write mechanisms proceeded, it became evident that there was insufficient direct knowledge about the reaction systems or general knowledge about the mode of formation of metal-to-metal bonds to allow a reasonable sequence to be written . As a result, this section will be an attempt to summarize what is known about the systems and raise questions regarding what is not well understood. In this way, it is hoped that attention will be focused upon areas needing further research.

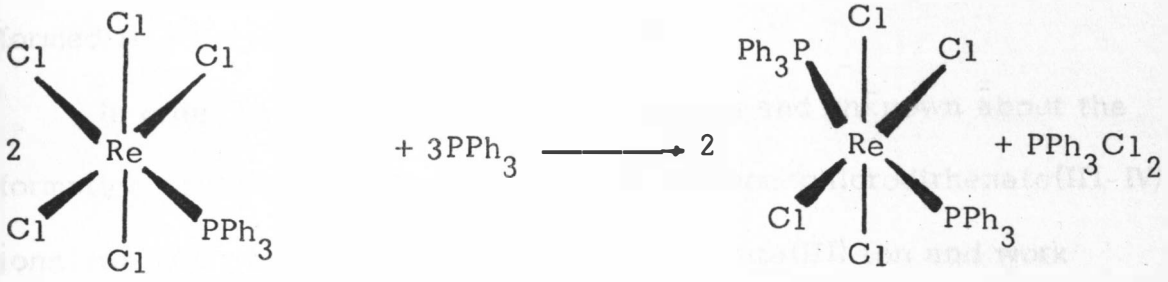
Essential to this discussion is the fact that rhenium(V) chloride is a dimer, with little or no interaction between the rhenium atoms. It should also be recalled that in the reaction of rhenium(V) chloride, triphenylphosphine, and acetone, the relative absence of water seemed to favor the formation of tetrachlorobis(triphenylphosphine)rhenium(IV) and 1,1-dimethyl-3-oxobutyltriphenylphosphonium pentachlorotriphenylphosphinerhenate(IV) while some water in the system favored the formation of oxotrichlorobis(triphenylphosphine)-rhenium(V) and bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium)

nonachlorodirhenate(III-IV).

The formation of the tetrachlorobis(triphenylphosphine)-rhenium(IV) may be rationalized by the following:







The difficulties become apparent, when one attempts to write a similar route for the formation of the pentachlorotriphenylphosphinerhenate(IV) ion.

$$Re_2Cl_{10} + 2\ Me_2CO \longrightarrow 2ReCl_5(Me_2CO)$$

$$2ReCl_5(Me_2CO) + 2PPh_3 \longrightarrow 2ReCl_5PPh_3$$

Here we have pentachlorotriphenylphosphinerhenium(V), but not the ion, and it is here that the first of many difficulties regarding a complete discussion of this system became apparent. How is pentachlorotriphenylphosphinerhenium(V) reduced to form the ion?

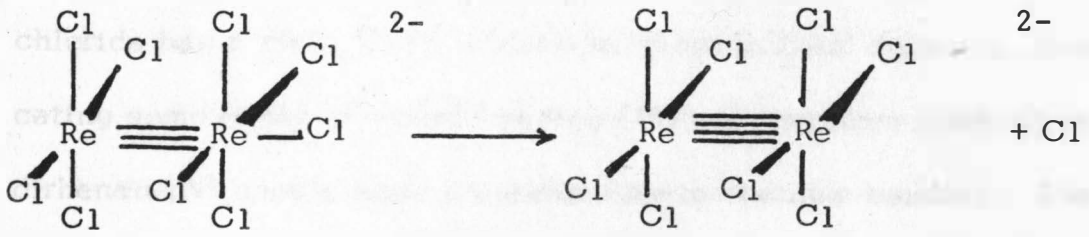
The formation of the oxotrichlorobis(triphenylphosphine)-rhenium(V) can easily be accounted for by the scheme of Grove and Wilkinson (34):

$$ReCl_5 + H_2O \longrightarrow (ReOCl_3) + 2HCl$$

$$(ReOCl_3) + 2PPh_3 \longrightarrow ReOCl_3(PPh_3)_2$$

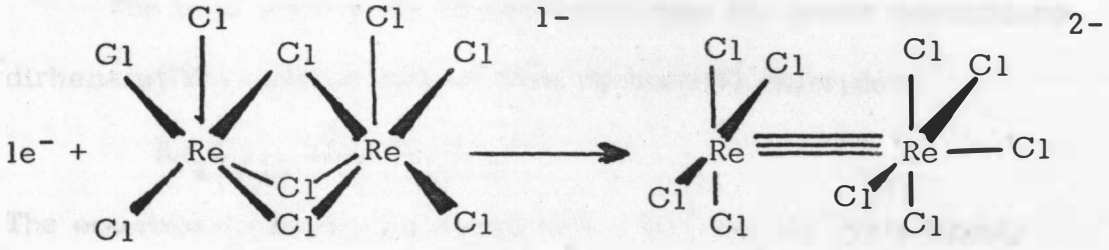
This scheme readily accounts for the fact that the amount of product formed is a function of the water present.

In order to better present what is known and unknown about the formation of the octachlorodirhenate(III) and nonachlorodirhenate(III-IV) ions, we will begin with the octachlorodirhenate(III) ion and work backwards. There is much evidence that the octachlorodirhenate(III) ion obtained in the systems under consideration arises from conversion of the nonachlorodirhenate(III-IV) ion:



Though the structure of nonachlorodirhenate(III-IV) is unknown, it has been suggested (36), (44) that the ion has the structure shown. The conversion would require the loss of the axial chlorine atom. The loss of a chlorine atom, rather than an ion, does not seem too likely.

Although the nonachlorodirhenate(III-IV) ion has been reported several times, the precursor seems to be the nonachlorodirhenate(IV) ion obtained by Bonati and Cotton (44) from a system different than ours. They suggest that this ion may have the structure of rhenium(IV) chloride:



Such a conversion has several redeeming features. Rhenium(IV) chloride has a short (2.74 A) rhenium-rhenium bond distance, indicating some metal-to-metal bonding (45) and therefore nonachlorodirhenate(IV) should have some rhenium-to-rhenium bonding. The rhenium-rhenium bond is quite stable and this ought to provide driving force for the reaction to occur. Also, as was (45) pointed out, lowering the oxidation state of rhenium below four seems to highly favor the formation of rhenium-to-rhenium bonds.

In the conversion given, the question arises as to what is the reducing agent. In the system of Bonati and Cotton (44), a metal such as copper performs the task. In the rhenium(V) chloride system the reducing agent is not as evident. Disproportionation may be the cause, but just how this is accomplished is not apparent. Also, triphenylphosphine may be the reducing agent.

The next problem is to determine how the green nonachlorodirhenate(IV) could be formed from rhenium(V) chloride:

$$Re_2Cl_{10} \xrightarrow{?} Re_2Cl_9^{1-} + X$$

The equation is easily balanced if X = Cl^+ but Cl^+ is a highly unusual species and it is very difficult to account for its formation in such a system.

This series of reactions should emphasize both the known and unknown points about the system. In particular, the structures of the

nonachlorodirhenate(III-IV) and nonachlorodirhenate(IV) would help in reaching a more thorough understanding of the system. In addition, it should be emphasized that, while Bonati and Cotton (44) have shown that the nonachlorodirhenate(III-IV) ion is obtained from the nonachlorodirhenate(IV) ion in their sequence of reactions, there is no direct evidence for the nonachlorodirhenate(IV) ion in the rhenium(V) chloride system. It has been considered in such a context because it would seem to be a reasonable intermediate in passing from rhenium(V) chloride, with no metal-to-metal bonding, to nonachlorodirhenate(III-IV), presumably with strong rhenium-to-rhenium bonds. Further, it is obvious that a closer understanding of the oxidation-reduction mechanism in the system is required. It will be necessary to obtain information as to the structure of rhenium(V) chloride in acetone and determine whether or not it reacts with the acetone.

There are indications that one of the most important reactions to be considered is that of the action of water in varying amounts on the rhenium(V) chloride. In water or alkali, rhenium(V) chloride forms rhenium(IV) oxide and perrhenate (7) and the reaction can be written as the disproportionation:

$$3Re^{V} \longrightarrow 2Re^{IV} + Re^{VII}.$$

However, Allen, et al. (38) observed the formation of nonachloro-

dirhenate(III-IV) and perrhenate in an acetone-water solution of rhenium(V) chloride. This may be written as:

$$7Re^{V} \longrightarrow 2(Re^{IV}\text{-}Re^{III}) + 3Re^{VII}.$$

Grove and Wilkinson (34) claim that oxotrichlororhenium(V) is formed when rhenium(V) chloride is dissolved in moist acetone. This implies that less water was available than in Allen's (38) system, although a quantitative measurement is not possible because Grove and Wilkinson made no measurements of the water content. They further postulate that, with an excess of hydrogen chloride available,

$$(ReOCl_3) + 2HCl \longrightarrow H_2ReOCl_5.$$

The oxopentachlororhenate(VII) ion was obtained when rhenium(V) chloride was dissolved in 12N hydrochloric acid. It remains to be seen whether or not such a reaction would take place in an acetone-hydrogen chloride system containing rhenium(V) chloride.

It would seem that the products formed from the hydrolysis of rhenium(V) chloride vary according to the system and particularly the amount of water available. Further, from the observation that in our system the oxotrichlorobis(triphenylphosphine)rhenium(V) and the nonachlorodirhenate(III-IV) ion are formed together, and Allen's system (38), where perrhenate and nonachlorodirhenate are produced, it seems that the action of water on rhenium(V) chloride can promote

the formation of the dinuclear ion, in addition to forming the usual oxygenated species. Also, it should be pointed out that the rhenium(V) chloride-acetone solutions have been observed in our laboratory and by others (34), (38) to be green at first and only gradually turn purple. This indicates that, although the oxygenated species is formed very rapidly as shown by the rapid precipitation of the oxotrichlorobis(triphenylphosphine)rhenium(V) , the formation of the nonachlorodirhenate(III-IV) ion is formed much more slowly. One further observation is the presence of less water in the system of rhenium(V) chloride and triphenylphosphine in acetone gave less nonachlorodirhenate(III-IV). Again, the water seems implicated in the formation of this species and it seems worthwhile to repeat that one of the important steps in an understanding of the behavior of rhenium(V) chloride in solution will be taken when a complete elucidation of the action of the water is given.

The role of the solvent seems to be important. In the more polar solvents, such as acetone and acetonitrile, most of the isolatable products are monomers, while in benzene, the products are dimeric in nature. Benzene did not seem to react when used as a solvent in the rhenium(V) chloride-triphenylphosphine system. Because of that and the fact that it seemed to allow exclusive formation of dimeric products, it may well be best suited for a close study

of rhenium's penchant for homophilicity (90).

SUMMARY

The reactions of rhenium(V) chloride and triphenylphosphine in several solvents have been investigated and the products characterized. In several cases, independent methods of syntheses were carried out to provide additional proof of the nature of the products.

In acetone, the reaction of triphenylphosphine and rhenium(V) chloride yielded oxotrichlorobis(triphenylphosphine)rhenium(V) and tetrachlorobis(triphenylphosphine)rhenium(IV). Their relative yields depended upon reaction conditions. The mother liquor yielded 1,1-dimethyl-3-oxobutyltriphenylphosphonium pentachlorotriphenylphosphinerhenate(IV) and a mixture of bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) nonachlorodirhenate(III-IV) and bis-(1,1-dimethyl-3-oxobutyltriphenylphosphonium) octachlorodirhenate(III). Complicating the identification of the products was the unusual role the solvent played in the formation of the last three compounds.

Although the rhenium(V) chloride is dimeric in the solid, products obtained were mainly monomeric. This attests to the ability of the acetone to break the rhenium-chlorine bonds found in rhenium(V) chloride and prevent the formation of the strong rhenium-rhenium bonds. The occurrence of the relatively small amount of the dimeric species

is of considerable interest, however, and many questions regarding its formation remain unanswered.

The reaction of rhenium(V) chloride with pyridine gave dioxotetrakis(pyridine)rhenium(V) chloride dihydrate as the only product, while the reaction of rhenium(V) chloride and triphenylphosphine in acetontrile gave tetrachlorobis(triphenylphosphine)rhenium(IV). Both of these products had been reported previously, although from slightly modified systems.

The reaction of rhenium(V) chloride and triphenylphosphine in benzene gave two identifiable products, neither monomeric in nature. The first was bis(triphenylphosphonium) nonachlorodirhenate(III-IV) while trichloro(triphenylphosphine rhenium(III) was obtained when the mother liquor was concentrated. The fact that no monomeric products were obtained indicated that benzene was unable to prevent formation of the rhenium-rhenium bond.

The reaction of triphenylphosphine oxide and rhenium(V) chloride in acetone gave only the compound, bis[μ-hydrogenbis(triphenylphosphine oxide)] nonachlordirhenate(III-IV). The symmetrically bonded proton provided the key to understanding the infrared spectrum. Location of the proton in an nmr spectrum would be good on confirming proof but lack of solubility of the product prevented this.

The reaction of triphenylphosphine with rhenium(V) chloride in carbon tetrachloride gave a very small amount of an unidentified product.

The formulation of several of the products from the reaction of rhenium(V) chloride and triphenylphosphine in acetone as phosphonium salts led to a synthesis of the hydrogen dichloride and bromide salts of 1,1-dimethyl-3-oxobutyltriphenylphosphonium cation. The study of the nmr spectra of the 1,1-dimethyl-3-oxobutyltriphenylphosphonium and 1-methyl-3-oxobutyltriphenylphosphonium hydrogen dichloride salts agreed with the literature.

Investigation of the infrared spectrum of bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) hexachlororhenate(IV) led to a careful investigation of a series of hexachlororhenate(IV) far infrared spectra and in particular, the asymmetric rhenium-chlorine stretching mode. The asymmetric shape of the peak is most likely due to a lowering from octahedral symmetry of the anion. It was found that factors such as sample preparation, scan speed, etc. can affect the position of the peak.

APPENDIX

The infrared absorption spectra are listed in cm^{-1} with their relative intensities as follows:

vw - very weak

w - weak

m - medium

s - strong

vs - very strong

shld. - shoulder

The potassium bromide used in obtaining the spectra showed two bands 3420 cm^{-1} and 1630 cm^{-1} which presumably were due to the presence of water.

Table VI.
Infrared Absorption Maxima for Tetrachlorobis(triphenylphosphine)rhenium(IV).

Wave Number(cm^{-1})	Intensity	Wave Number(cm^{-1})	Intensity
3420	w	1089	s
3050	w	1075	shld.
2315	vw	1030	w
1952	vw	998	m
1886	vw	925	vw
1806	vw	835	vw
1662	vw	736	vs
1582	w	698	shld.
1568	w	685	vs
1480	s	610	vw
1420	vs	540	vw
1380	vw	525	vs
1325	shld.	505	m
1310	w	490	m
1275	vw	445	w
1190	w	420	vw
1158	w	317	s

Table VII.
Infrared Absorption Maxima for 1,1-Dimethyl-3-oxobutyltriphenylphosphonium Pentachlorortriphenylphosphinerhenate(IV).

Wave Number(cm^{-1})	Intensity	Wave Number(cm^{-1})	Intensity
3410	w	1100	s
3058	w	1087	shld.
2980	vw	1070	shld.
1960	vw	1030	w
1900	vw	999	m
1815	vw	940	w
1710	s	850	vw
1610	vw	750	s
1585	w	720	m
1575	vw	695	vs
1483	s	675	shld.
1436	vs	585	w
1388	w	540	shld.
1370	w	535	s
1360	w	520	m
1340	w	499	m
1190	w	450	w
1180	w	341	w
1172	shld.	311	vs
1130	w	290	w

Table VIII.
Infrared Absorption Maxima for Bis(1,1-dimethyl-3-oxotributyltriphenylphosphonium) Nonachlorodirhenate(III-IV) and Bis-(1,1-dimethyl-3-oxobutyltriphenylphosphonium) Octachlorodirhenate(III).

Wave Number(cm^{-1})	Intensity	Wave Number(cm^{-1})	Intensity
3420	w	1100	vs
3060	w	1075	shld.
2990	w	1020	vw
2940	vw	998	m
1980	vw	940	w
1820	vw	845	vw
1720	vs	755	shld.
1620	vw	749	s
1585	w	720	vs
1570	vw	701	s
1485	m	690	vs
1460	w	670	vw
1440	vs	612	vw
1390	w	580	w
1360	w	535	vs
1340	w	505	m
1320	shld.	460	w
1270	vw	440	w
1190	w	340	shld.
1170	w	331	vs
1125	w	300	shld.

Table IX.
Infrared Absorption Maxima for Oxotrichlorobis(triphenylphosphine)-rhenium(V).

Wave Number(cm^{-1})	Intensity	Wave Number(cm^{-1})	Intensity
3420	vw	969	vs
3042	w	920	vw
1960	vw	845	vw
1885	vw	749	vs
1870	vw	705	s
1865	vw	691	vs
1585	w	602	vw
1570	w	515	vs
1473	s	499	s
1423	vs	490	shld.
1380	shld.	442	w
1335	vw	435	shld.
1315	w	400	vw
1190	m	330	shld.
1160	w	325	shld.
1092	vs	316	m
1070	shld.	300	shld.
1030	w	268	w
998	m		

Table X.
Infrared Absorption Maxima for Dioxotetrakis(pyridine)rhenium(IV) Chloride Dihydrate.

Wave Number(cm^{-1})	Intensity	Wave Number(cm^{-1})	Intensity
3420	w	1200	vw
3220	w	1160	v
3175	vw	1070	s
3100	shld.	1050	w
3070	m	1005	vw
1945	vw	950	vw
1860	vw	820	vs
1740	vw	765	vs
1710	vw	755	shld.
1635	m	745	shld.
1610	s	695	vs
1560	vw	680	s
1537	s	650	w
1480	vs	480	w
1450	vs	400	w
1360	w	340	vw
1345	w	301	vs
1330	w	296	vs
1240	w	277	shld.
1215	s		

Table XI.
Infrared Absorption Maxima for Bis[μ-hydrogen-bis(triphenylphosphine oxide)] Nonachlorodirhenate(III-IV).

Wave Number(cm^{-1})	Intensity	Wave Number(cm^{-1})	Intensity
3410	vw	1105	shld.
3050	w	1065	w
2210	vw	1025	w
1970	vw	1000	w
1900	vw	995	vw
1810	vw	910	m,broad
1585	m	750	m
1575	w	722	vs
1480	m	690	vs
1435	vs	610	w
1390	vw	540	vs
1335	vw	490	w
1310	w	445	w
1250	w	365	w
1180	shld.	324	vs
1160	w	285	vw
1120	vs		

Table XII.
Infrared Absorption Maxima for 1-Methyl-3-oxobutyltriphenylphosphonium Hydrogen Dichloride.

Wave Number(cm^{-1})	Intensity	Wave Number(cm^{-1})	Intensity
3460	s	1160	s
3370	s	1102	vs
3025	w	1020	w
2990	w	995	m
2910	w	900	w
2480	w	835	w
2150	m	740	vs
1705	vs	720	vs
1635	w	685	vs
1585	w	530	vs
1480	m	500	w
1435	s	470	w
1420	shld.	405	vw
1380	w	360	w
1360	m	290	vw
1320	w	250	vw
1210	m		

Table XIII.
Infrared Absorption Maxima for Bis(triphenylphosphonium) Nonachlorodirhenate(III-IV).

Wave Number(cm^{-1})	Intensity	Wave Number(cm^{-1})	Intensity
3410	vw	1075	vw
3060	w	1030	w
2920	vw	1000	w
2385	m	925	shld.
1975	vw	900	shld.
1905	vw	880	m
1820	vw	745	s
1705	w	720	s
1610	vw	690	vs
1590	m	675	shld.
1575	shld.	610	vw
1485	m	540	w
1440	vs	500	vs
1340	w	430	w
1320	w	400	vw
1190	w	326	vs
1165	w	300	shld.
1110	vs		

Table XIV.
Infrared Absorption Spectrum of Trichloro(triphenylphosphine)-rhenium(III).

Wave Number(cm^{-1})	Intensity	Wave Number(cm^{-1})	Intensity
3410	w	1160	m
3050	w	1090	vs
2960	vw	1070	vw
1960	vw	1025	w
1890	vw	998	m
1815	vw	840	vw
1640	vw	745	vs
1600	w	705	s
1585	w	685	vs
1570	w	612	w
1480	s	525	vs
1430	vs	500	s
1420	shld.	445	w
1380	shld.	415	vw
1330	vw	345	s
1310	vw	305	m
1190	m		

Table XV.
Infrared Absorption Maxima for Product from the Reaction of Rhenium(V) Chloride and Triphenylphosphine in Carbon Tetrachloride.

Wave Number(cm^{-1})	Intensity	Wave Number(cm^{-1})	Intensity
3410	vw	1070	shld.
3050	w	1025	m
1960	vw	1000	m
1895	vw	970	w
1815	vw	850	w
1770	vw	780	shld.
1590	m	745	s
1560	vw	722	s
1550	vw	690	vs
1480	s	610	vw
1435	vs	540	vs
1380	vw	530	vs
1340	m	525	shld.
1280	w	500	m
1180	shld.	440	w
1140	vs	420	w
1120	vs	315	s
1090	vs	300	shld.

Table XVI.
Infrared Absorption Maxima for Bis(tetraphenylphosphonium) Hexachlororhenate(IV).

Wave Number(cm^{-1})	Intensity	Wave Number(cm^{-1})	Intensity
3460	vw	1270	vw
3140	vw	1185	s
3060	m	1160	m
3020	shld.	1100	vs
2200	w	1020	w
1995	w	990	vs
1970	w	940	vw
1925	w	925	vw
1900	w	840	w
1825	w	760	vs
1780	w	750	vs
1700	w	715	vs
1680	w	685	vs
1610	w	610	m
1580	vs	530	vs
1575	shld.	445	w
1480	vs	430	vw
1435	vs	390	w
1410	shld.	335	vw
1390	shld.	300	shld.
1335	m	290	vs
1310	m	275	shld.

Table XVII.
Infrared Absorption Maxima for Bis(1,1-dimethyl-3-oxobutyl-triphenylphosphonium) Hexachlororhenate(IV).

Wave Number(cm^{-1})	Intensity	Wave Number(cm^{-1})	Intensity
3420	w	1170	w
3060	w	1136	w
2995	w	1100	vs
2910	vw	1075	shld.
2000	vw	1020	shld.
1910	vw	995	s
1830	vw	940	w
1820	vw	850	vw
1718	vs	752	s
1620	w	719	vs
1582	m	700	vs
1570	w	695	shld.
1510	w	665	vw
1471	m	612	vw
1460	w	580	m
1435	s	532	vs
1389	w	501	m
1369	shld.	460	vw
1359	w	425	w
1340	w	302	shld.
1215	vw	294	vs
1190	w	279	shld.

Table XVIII.
Infrared Absorption Maxima for (1,1-Dimethyl-3-oxobutyl-(triphenylphosphonium) Hydrogen Dichloride.

Wave Number(cm^{-1})	Intensity	Wave Number(cm^{-1})	Intensity
3410	vw	1165	w
3050	vw	1120	w
2910	w	1100	s
2860	vw	1025	vw
2000	vw	998	m
1940	vw	950	w
1820	vw	870	m
1705	vs	760	s
1585	w	740	s
1570	vw	710	s
1480	m	695	s
1460	vw	610	m
1435	vs	580	m
1390	vw	530	vs
1360	vw	500	s
1335	vw	425	w
1190	w	410	w
1175	w		

Table XIX.
Infrared Absorption Maxima for Bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) Nonachlorodirhenate(III-IV).

Wave Number(cm^{-1})	Intensity	Wave Number(cm^{-1})	Intensity
3410	w	1185	w
3060	w	1160	w
2980	w	1120	w
2930	vw	1100	vs
2000	vw	1070	vw
1910	vw	992	m
1882	vw	935	w
1715	vs	840	vw
1620	vw	745	s
1580	m	718	vs
1570	shld.	695	vs
1480	s	685	shld.
1450	w	660	w
1432	vs	610	w
1410	vw	575	m
1385	w	530	vs
1370	vw	498	m
1350	w	425	vw
1330	w	325	vs
1310	vw	310	shld.
1265	vw		

Table XX.
Ultraviolet and Visible Absorption Maxima and Molar Extinction Coefficients.

1,1-Dimethyl-3-oxobutyltriphenylphosphonium Pentachlorotriphenylphosphinerhenate(IV).

Wave length mμ	Molar Extinction Coefficient
430	8.20×10^2 l mole^{-1} cm^{-1}
378	2.26×10^3
320	2.96×10^3
290	4.72×10^3
277	8.58×10^3
270	1.02×10^4

Bis(triphenylphosphonium) Nonachlorodirhenate(III-IV).

Wave length mμ	Molar Extinction Coefficient
700	1.47×10^3 l mole^{-1} cm^{-1}
538	9.74×10^2
355	5.16×10^3
320	9.18×10^3
277	2.04×10^4
269	2.04×10^4
262	1.90×10^4

Bis[μ-hydrogen-bis(triphenylphosphine oxide)] Nonachlorodirhenate-(III-IV).

Wave length mμ	Molar Extinction Coefficient
695	3.43×10^3 l mole^{-1} cm^{-1}
530	2.70×10^3
355	1.35×10^4
320	2.83×10^4
272	5.76×10^4
265	6.50×10^4
250	5.24×10^4

Table XXI.
Ultraviolet and Visible Absorption Maxima and Molar Extinction Coefficients.

Bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) Nonachlorodirhenate(III-IV) and Bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) Octachlorodirhenate(III).

Wave length mμ	Molar Extinction Coefficient*
695	0.40
550	0.10
315	0.66
277	0.93
270	1.00
263	0.95

Bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) Nonachlorodirhenate (III-IV).

Wave length mμ	Molar Extinction Coefficient
710	1.17×10^3 l mole^{-1} cm^{-1}
530	9.60×10^2
353	4.92×10^3
318	5.66×10^3
277	2.55×10^4
270	2.17×10^4
264	1.37×10^4

* relative values

Table XXII.

d Values for Bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) Nonachlorodirhenate(III-IV).

d Values	Intensity	d Values	Intensity
11.78	70	5.12	60
10.40	1	4.06	1
9.71	98	3.85	.05
8.34	100	3.66	1
6.86	5	3.31	.05
6.15	90	2.21	2
5.53	5	2.11	2

d Values for Bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) Octachlorodirhenate(III).

d Values	Intensity	d Values	Intensity
11.04	70	4.53	1
8.75	1	4.15	1
7.89	1	3.80	2
6.60	98	3.45	1
5.98	100	3.16	1
5.15	40		

Table XXIII.
d Values for 1,1-Dimethyl-3-oxobutyltriphenylphosphonium Pentachlorotriphenylphosphinerhenate(III).

d Values	Intensity	d Values	Intensity
12.99	80	3.39	20
8.83	10	3.16	1
6.46	25	3.07	.05
6.06	100	2.99	.05
5.64	40	2.86	60
5.01	95	2.72	1
4.46	15	2.64	2
4.27	15	2.45	5
4.13	2	2.38	5
3.99	10	2.31	5
3.53	10		

Table XXIV.
d Values for the Mixture of Bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) Nonachlorodirhenate(III-IV) and Bis(1,1-dimethyl-3-oxotriphenylphosphonium) Octachlorodirhenate(III).

d Value	Intensity	d Value	Intensity
11.78	95	4.39	.05
9.11	1	4.19	1
6.86	98	4.02	.05
6.12	100	3.86	2
5.27	80	3.49	1
4.56	1		

Table XXV.
Nuclear Magnetic Resonance Chemical
Shift and Coupling Constant Data.[a]
(Chemical Shifts Relative to TMS, Internal)

1,1-Dimethyl-3-oxobutyltriphenylphosphonium Pentachlorotriphenylphosphinerhenate(IV).

Chemical Shift, ppm	Coupling Constant, H_z
1.68 (d,6H)	J = 19H_z
2.08 (s,3H)	
2.80 (d,2H)	J = 9H_z
7.70 (m,30H)	

Bis(1,1-dimethyl-3-oxobutyltriphenylphosphonium) Hexachlororhenate(IV) (Solvent CD_3CN, 0.72M, solvent $CDCl_3$, 1.0M).

Chemical Shift, ppm	Coupling Constant, H_z
1.7 (d,6H)	J = 19H_z
2.1 (s,3H)	
3.1 (d,2H)	J = 9H_z
7.7 (m,15H)[b]	
12.3 (s,1H)	

1,1-Dimethyl-3-oxobutyl(triphenylphosphonium) Hydrogen Dichloride (Solvent CD_3CN, 0.07M).

Chemical Shift, ppm	Coupling Constant, H_z
1.8 (d,6H)	J = 20H_z
2.1 (s,3H)	
2.8 (d,2H)	J = 9H_z
7.7 (m,15H)[b]	

Table XXV (Con't).
1-Methyl-3-oxobutyltriphenylphosphonium Hydrogen Dichloride (Solvent CD_3CN).

Chemical Shift, ppm	Coupling Constant, H_z
1.4 (q,3H)	J = 20H_z
2.3 (s,3H)	
3.1 (d,2H)	J = 7H_z
4.5 (m,1H)	
7.8 (m,15H)[b]	
11.0 (s,1H)	

a) Chemical shifts relative to TMS (internal); b) Center of complex multiplet.

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